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A RUDIMENTARY TREATISE

ON THE

METALLURGY OF SILVER AND LEAD,

CONTAINING A

DESCRIPTION OF THE ARGENTIFEROUS AND PLUMBIFEROUS
MINERALS; THE METHODS OF ASSAYING THEM;

AND

THE PROCESSES IN USE IN VARIOUS PARTS OF THE WORLD
FOR TREATING THE ORES OF SILVER AND LEAD FOR
THEIR VALUABLE CONSTITUENTS;

TOGETHER WITH HISTORICAL AND STATISTICAL NOTICES
OF THE TWO METALS.

BY

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PREFACE.

IN the preparation of this volume I have sought to give a general view of the present condition of the metallurgy of silver and lead. In order to do this efficiently, the subject has been arranged in such a manner that those processes having a close similarity in their chemical features, in the apparatus employed, and the results sought to be obtained, are grouped together.

Thus it will be seen that the various methods of amalgamation have been described in succession, although they belong to different hemispheres. The same may be said of the methods of treating sulphide of lead in hearths. The three methods of reducing lead ores in reverberatory furnaces by double decomposition have been given in a single chapter, although the three methods described are peculiar to as many various nations. And the processes of Augustin, Ziervogel, and Von Patera, have been placed side by side, although now in operation at very different localities.

During the thirty months just passed I have resided in or visited the most important metalliferous regions of Central Europe, and have had an opportunity of

seeing in operation the greater number of the processes that I have described, and in several instances have enjoyed the friendship of the inventors or improvers of the processes in question. In looking back upon this period spent among practical European miners and metallurgists, I cannot but regret that it is now drawing to a close; for I have found them, almost without exception, earnest, thoughtful men, in whose sterling characters the noble qualities of their calling were reflected. To enumerate the names of those to whom I am indebted for information would trespass too widely upon my present limits, though I cannot omit to mention the officers of the royal smelting establishment of Saxony at Freiberg, those of Hanover at Clausthal and in the vicinity, and those of the imperial furnace at Joachimsthal, in Bohemia.

Among the English, American, German, and French works that I have found very valuable, are those of Rivot, Scheerer, Karsten, Plattner, Kerl, Phillips, Mitchel, Graham, Darlington, Dana, Whitney, Pelouse, and Fremy, and the excellent statistics collected and arranged by Mr. Hunt, of the Government School of Mines.

Finally, in presenting this little work to the public, I cannot refrain from expressing my gratification at the flattering reception given to the "Treatise on the Metallurgy of Copper," which was issued by Mr. Weale some few months ago.

May 15, 1861.

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THE METALLURGY OF SILVER AND LEAD.

PART I.

HISTORICAL SKETCHES OF SILVER AND LEAD ; PHYSICAL AND CHEMICAL PROPERTIES ; MINERALOGICAL DESCRIPTION OF THE ORES, AND THE VARIOUS METHODS OF ASSAYING SUBSTANCES CONTAINING THE TWO METALS.

CHAPTER I.

HISTORICAL SKETCH OF SILVER.

SILVER had already taken a high rank among the metals in the days of Abraham, and even at that early period we find it playing the same part in the economy of nations that gives it so much importance to us of the present day. It was a standard of value, and a medium for the transaction of exchanges when first mentioned; this is still its chief function, and will probably continue to be as long as mankind buy and sell.

In the time of the patriarchs it would appear that money, as we understand it, was already but partially in use; since sometimes we read of Abraham receiving so many *pieces* of silver, and at others that he *weighed* out a certain number of shekels of the same metal. Hence we may conclude that the plan of employing

a piece of determined size in commercial transactions, was only then superseding the more ancient system of determining, by a separate weighing, the amount of silver necessary in each exchange.

Whether these *pieces* were stamped with a device or not we have no means of knowing, but that silver as well as gold was at that period wrought into various household utensils and articles of ornament, we have abundant evidence in the book of Genesis.

There is a passage in the account of the purchase of the field of Hebron which, in investigating the ancient history of silver, demands more than our passing attention. It is the statement that the silver weighed by Abraham was *current money with the merchants*. This leads to the conclusion that various sorts of silver were already recognised, and that the merchants possessed the knowledge necessary to distinguish between the current and the uncurrent, or the pure and alloyed; in short, that the rudiments of assaying were practically understood.

Numismatologists concur in considering the oldest stamped money that has come down to us to be that made from silver by the Æginetans, and in the Parian chronicle the origin of coined money is ascribed to that nation, the date of its discovery being placed in the time of Phidon, who reigned 895 years before the Christian era. Homer's heroes carried weapons ornamented with silver, and that bard even mentions the locality from whence the precious substance was brought; but where to search upon modern maps for the region thus made known by name will probably continue to be, as it now is, an unsolved problem for the antiquary.

It is generally supposed that the silver possessed by the nations along the eastern end of the Mediterranean came from some country to the north or east, and Chaldea, Bucharía, and the mountains belonging to the modern Russian Empire have been mentioned as probable localities. That silver was abundant in early historical times is clear from the vast quantities that were obtained by conquering armies in the form of plunder, ransom, or tribute. Thus Rawlinson has found on a Babylonian monument an inscription stating that the city of Damascus, after its conquest by Phuluk, was adjudged to pay a tribute of 2300 talents of silver, beside gold, copper, and brass; and if it were possible to credit the figures of Pliny, Cyrus obtained from his conquests in Asia an amount of silver equivalent to 7,720,000,000*l.*; while according to Herodotus, the nations subdued by the Persians, excepting the Indies and Antioch, paid a yearly tribute in silver of about 3,000,000*l.*

The metallic treasures of the East, won from the degenerate successors of Alexander by vigorous Roman warriors, flowed steadily into the lap of the Mistress of the World, where they joined the precious streams coming northward from the coffers of the sumptuous Carthaginians. For fifty years after the second Punic war, the conquered city paid an annual tribute of 9000 pounds of silver. This treasure was partly collected in the hands of private individuals or families, and partly in the public treasury. The latter is said to have received, during the nine years following the second Punic war, 112,000 pounds of silver from Spain alone. The spectacles of the Emperors were often accompanied by the most lavish display of metallic wealth. To such an extent was

this carried, that Caligula, we are told, loaded 124,000 pounds of silver upon the armour and weapons that he caused to be brought into the circus. Indeed, the extraordinary accounts given by various classic authors of the amount of silver collected in ancient Rome, would often have the appearance of gross exaggeration, were we not aware that the treasures of the world gathered for generations within her walls; and had we not incontestable statistics of the products of a region that in modern times has yielded treasures far exceeding those possessed by Rome even in the most brilliant period of her decadence:—I allude to the meridional countries of the new world, which will claim our attention presently.

The localities from whence the ancients obtained their silver seem to have been quite numerous. The mines of Laurium, which Eschylus calls the “fountain of silver ‘treasure of the earth,” were possessed by the Athenians: their production appears to have largely decreased in early days, so that Strabo speaks of them as exhausted.

Diodorus relates that the shepherds on the Pyrenees having set fire to their forests, the silver in the earth was fused and ran upon the ground in numerous streams, and that the natives not knowing the value of the extraordinary substance thus springing from their mountains, exchanged it with the Phœnician traders for wares of small value. Pliny writes, what we may believe with less extension of our credulity, that in his time the miners of Spain sought silver in the bowels of the earth a mile and a half beyond the light of day. The Carthaginians, according to Polybius, had 40,000 men engaged in the Spanish mines, and

the Moors are known to have continued the search that had in turn yielded so largely for nearly all the great nations of antiquity; yet when, in 1571, the German family of Fugger re-opened the deserted veins, they succeeded in the space of thirty-six years in taking out more than 3,000,000*l.* worth of the precious metal.

Thus from the most remote periods, strangers have sought in Spain the silver which the natives allowed to remain dormant in the earth. Nor is this rule at present reversed, since by royal decrees of 1825 and 1849 the mines were thrown open to foreign enterprise, and several English companies are now exploring districts that were wrought in the grey antiquity, perhaps for the merchants of Tyre.

When Rome lost her proud precedence, her stores of silver and gold moved eastward toward the seat of the Byzantine Government, and the dark centuries that then followed were not of a character to favour mining or to preserve records of metallic discovery.

German fable carries the first opening of some of the middle European mines back to the seventh century. In the tenth century, according to records that appear quite reliable, silver mines existed in Bohemia; and in the twelfth century, Tyrolese mines were worked. From Bohemia mining knowledge and the spirit of mining enterprise spread to the countries toward the north and west; in the tenth century the mines of the Hartz were discovered, and in the twelfth those of Saxony were opened.

The mines of England, France, Hungary, and Norway were already in operation when the discovery of the new world, with its fabulous stores of metallic

wealth, opened a new epoch in the history of the precious metals.

It was the fortune of Spain to reach this land of gold and silver first, and to appropriate to herself not only the treasure then in the possession of the natives, but what was far more important, the districts where the strata still held untold millions.

The Incas of Peru drew their silver from the mines of Porco, but without any of those ingenious and expensive contrivances that miners of the present day bring to their aid. They sank no shafts, but simply drove adits horizontally upon the vein, and worked out the ore that happened to lie above the water level. Their processes of reduction were as primitive as their methods of mining. They had no idea of the virtues of quicksilver—a metal not at all rare in their land—but fused the ore in rude furnaces, so built upon the mountain side that the prevailing winds fanned the wasteful flames. No money circulated in their empire, but the precious metals were lavished upon the walls of their temples, so that the polished surfaces threw back brilliant images of their governing deities, the sun and the moon. The palaces of the Inca nobility were also gorgeously decorated. To such an extent was this carried, that it is recorded that the soldiers of Pizarro found, near Cuzco, three beams of silver each twenty feet long, one foot broad, and two to three inches thick, which were intended to form ornaments for a country seat then in process of erection. The unfortunate prince Atahualpa, when made prisoner by the conquerors, sought to obtain his liberty by offering rooms full of the precious metals as a ransom. The ornaments torn from the temples of the various deities,

and removed from the royal palaces by the loyal subjects who did not foresee the dark deed of treachery that awaited them, amounted to a value at that period of 3,500,000*l.* of gold and 51,610 marks,* or about 25,805 pounds of silver.

But the rapacious conquerors of the new world found but a comparatively small portion of the precious metals that their victories brought them into possession of, in the hands of the inhabitants. The veins of silver, discovered and undiscovered, held a treasure that could scarcely have been exceeded by their wildest dreams.

The silver production of the world is at the present time largely concentrated in the western hemisphere, and the richness and abundance of the ores of the Cordilleras and Andes promise a prize so tempting that almost continual revolution, and consequent insecurity of property, combined with the many difficulties which nature has thrown in the way, cannot prevent both native and foreign companies from pushing forward their precarious but often highly remunerative operations.

Peru is considered by Whitney to exceed all other countries in the vastness of its silver deposits, but the desolate region of snow and rock, in which some of the mines are situated, strikes even the most hardy miner with terror. The mines of Potosi are worked at a height even greater than that of Mont Blanc.

Among the richest silver mines in the world is that of Pasco, which was discovered by accident in 1630. It is so miserably worked that at one time 300 labourers were killed by the falling of a portion of the mine, and hence it is known as the Matagenti, or Kill-people. The well-known Cornish engineer, Richard Trevithick,

* Prescott's History of the Conquest of Peru.

introduced nine steam-engines into this mine; in 1814 he visited the country himself, and was received with the highest honours; it was even proposed to erect a statue to him in solid silver. In consequence of political dissension and civil war he was afterwards forced to escape, and he carried with him as the only remnant of his former wealth a single pair of silver spurs. The total amount of silver smelted at the Pasco works from 1784 to 1827 was 4,967,710 pounds troy, while the value of the metal yielded in 1851 was about 400,000*l.* sterling.

The Republic of Bolivia contains mines whose riches have passed into a proverb. The immense deposits in the isolated mountain known as the "Great Potosi," were discovered in 1545, since which date, according to various estimates, they have supplied the world with silver to the amount of 240,000,000*l.* The greatest store of metal appears to have been near the surface, so that the most flourishing period occurred shortly after they were opened. The average annual yield from 1545 to 1556 was about 2,318,000*l.*, and at that date silver possessed a value fully six times that which it holds at present. The Potosi mines, however, have fallen from their rank as the first in the world in point of quantity produced, and Chevalier estimates that at present they do not give an annual yield of over 192,000*l.*

The sad condition of the mining interest in Bolivia may be perceived, when the fact is mentioned that in that country in 1852 there were 4165 abandoned mines, and only sixty-six in actual operation. The mines of Peru and Bolivia, notwithstanding their depressed condition during recent years, yielded, from the period of their discovery to the year 1845, a quantity of silver equal

to 155,839,180 lbs. troy, or a money value of not less than 506,220,000*l*.

The political condition of Chili has been more favourable for the prosecution of mining adventure, and English enterprise has served to open a number of mines within its borders. Not less than 1,750,000 pounds of silver were raised in this country between 1846 and 1853.

The vast metallic deposits of Mexico began to claim attention about the same period as those of South America. Workings were commenced at Zacatecas in 1548, and at Guanaxuato in 1558. In the early period of their history the mines of Mexico produced, according to the estimates of Humboldt, from 400,000*l*. to 600,000*l*. per annum. During the 18th century this production gradually rose to 4,600,000*l*. per annum. This yearly sum decreased during the War of Independence, but within the last ten years it appears to have been higher than ever before, having, according to the most reliable accounts, reached 5,000,000*l*. sterling.

Chevalier calculates the total yield of the Mexican mines, between the advent of the whites and the year 1845, to be at least 162,858,700 pounds troy.

The earliest method of obtaining silver from its ores, of which we have any knowledge, bears an astonishing resemblance to that made use of at the present day. The reader will recall in this connection the striking similes used by the Prophet Ezekiel: "Son of man, the house of Israel is to me become dross: all they are brass, and tin, and iron, and lead, in the midst of the furnace; they are even the dross of silver." And, "As they gather silver, and brass, and iron, and lead, into the midst of the furnace, to blow the fire upon it, to melt it;

so will I gather you in mine anger and in my fury, and will leave you there and melt you." *

Only those who have seen beneath the glowing arch at the smelting works, flames surging wave after wave across the surface of the liquid metal carrying all the substances here called dross from the pure silver, and only those who have heard the roar of the fiery blast that ceases neither day nor night until its task of purification is accomplished, can appreciate the terrible force of the figure made use of by the prophet.

Several other passages in Holy Writ show us that the plan of extracting silver from its ores in those ancient times was first to obtain the silver in combination with lead and other easily oxidisable metals, and then, by heating the compound in a furnace and blowing air upon it, the impurities, or "dross," were turned into light oxides that were absorbed by the hearth, or floating on the surface were scraped away. The student of metallurgy will find that the method adopted in most of the silver furnaces of the present day, is in principle analogous to this.

The Romans made use of a similar plan. Strabo quotes Polybius as speaking of a silver ore which, after being washed seven times, was melted with lead, and became pure silver. Pliny says that most of the silver in his time was found in connection with lead, and he further remarks that neither metal can be extracted from its ores without the addition of the other.

The plans in use for extracting silver from its natural combinations, without in one form or another introducing lead into the furnace, are probably all of modern

* Ez. xxii. 18-20.

invention, and it is hence likely that this last expression of Pliny gives a general fact in the metallurgy of silver in his time. That silver must always be added to the ores of lead to insure the production of the latter metal is an error, probably originating in the circumstance that pieces of native silver, in order that they may be readily fused, are frequently given directly to the argentiferous lead in the process of cupulation. And it is further probable that in ancient times all the commercial lead contained a very perceptible quantity of silver which it might readily be supposed had been added purposely.

But it is not to be expected that very distinct accounts of the metallurgic processes of the Romans should have descended to us, since the reduction of ores was carried on in mountain fastnesses, far from regions frequented by men of cultivation; and mining and metallurgy were not then, as they have become in modern times, subjects to which men of the highest mental capacity directed their attention. What in later days such men as Swedenborg, Humboldt, Le Play, Rivot, and Scheerer have studied and written upon with laborious care, was then left almost entirely in the hands of serfs and malefactors. The accounts that Diodorus has handed down to us of the cruelties practised in the mines of Spain are shocking to every sense of humanity. Here the wretched labourers were driven, under the whip of overseers, night and day, along the dark passages of the mine, and forced to crawl with their loads of ore through cramped crevices charged with all the vapours that collect in subterranean excavations.

It is pleasing to one hopeful for the grand principle

of human progress to observe the immense and universal change for the better in the condition of the labourers, that has gradually taken place in this branch of industry. In England each precious life that is lost in the mines is counted with scrupulous care; and by governmental and private efforts it is sought to prevent accidents and save bodily suffering. In Westphalia I have seen vast bathing establishments, where all the miners belonging to the works may take their warm baths as regularly as did the old Roman ædile. The silver mines of Saxony have an organ at their mine to accompany them in their religious exercises that precede their hours of labour. In southern Austria I have found furnace-men and miners pensioned by the Government, at full pay, after a faithful service of 40 years, and in many lands steam not only draws the ore that was once laboriously carried out by human labour, but even transports the miner himself to and from his daily employment.

The mining of silver has led more than that of any other metal to this ameliorated condition of the miner, since its veins, penetrating deep into the earth, have carried the adventurer gradually forward, compelling him continually to devise new expedients for the purpose of raising the water that threatened to flood his treasure, to supply himself with pure air, and to draw to the surface the mineral that he collected in his rocky caverns. The study of Hydraulics, Pneumatics, and Mechanics was thus encouraged, by supplying a profitable field for the practical application of the results of these sciences. Gunpowder, which has wrought a change in the underground economy of the miner, as radical as that which it has effected in the

habits of civilised nations, is stated to have been first employed for blasting, in a mine producing silver; that of Rammelsberg in the Hartz.

The mines of silver are among the most extensive with which man has pierced the surface of the earth. A short time ago I read, at the bottom of the Samson mine, in Hanover, figures indicating that the main pit is 2,600 English feet, or within 40 feet of half a mile deep. It is a subject for wonder, how, with the aid of water power alone, and with wooden pumps that seem ready to fall to pieces with every stroke, even the most patient miner should have reached a depth so extraordinary. I have sought in vain for records of a mine that has been sunk to a point so far beneath the surface. The vein of Guanaxuato, in Mexico, has been explored for about 2,000 feet. The deeper mines about Clausthal on the Hartz reach 1,900 feet below the surface.

Some of the most extensive engineering works connected with mining have their origin in the search for silver.

The adit level, commenced in 1782 with the object of draining the Schemnitz district, in Hungary, is intended to be nearly 9 miles long, and each fathom it is estimated will cost 40*l*.

The Freiberg silver mines, in Saxony, are about to be tapped by a level nearly 8 miles (42,640 feet) in length, which will carry the water off at a point 410 feet below the level of the present deepest drainage. This tunnel will be 9 feet 11 inches in height, about 8 feet wide, and will rise in the whole distance 12·6 feet.

The metallic district of the Hartz around Clausthal

is drained by what is known as the "Tiefe Georgstollen," which was partly excavated in the latter years of the last century, and completed in 1835. It is $11\frac{1}{8}$ miles long, and taps the mines 840 feet below the surface. At a depth of 375 below the "Stollen" above mentioned, is a subterranean canal, upon which ore is transported in boats from different mines to a convenient place for winding. The length of this navigable channel is over two and a half miles.

Beside stimulating mankind to the profound study of the Divine laws by which matter is governed, by furnishing a domain where knowledge thus gained could be brought into daily and profitable use, silver, in its purified condition, has played among the nations of the earth a very important part as a civiliser. I allude to its employment in the form of money in facilitating necessary exchanges of property, and thus encouraging the ennobling intercourse of nations.

Mention has been already made of the period when it is supposed that coins were invented. From the earliest historical times to the present, silver has been *par excellence* the metal of the mint, and in pieces of determined value it now circulates under a thousand familiar names wherever commerce is known.

As a standard of value silver possesses advantages over all other substances. Gold alone presents qualities that can be brought into comparison with it in this connection. The fact that since the discovery of America gold has fallen, when compared with the necessities of life—as, for example, food—but in the proportion of 4 to 1, while silver in the same period has experienced a depression in the proportion of 6 to 1, has been adduced to show that the former

metal is the most stable in its worth, and hence best suited for a standard. But the circumstances that have taken place within the last century can never occur again. No virgin hemisphere yet remains with mountains teeming with silvery ores, whose discovery can work a new epoch in the history of the precious metals. But, as a substance of universal distribution in nature, and requiring long, laborious, and ingenious processes to extract it from its layer in the solid rock, and bring it into a form adapted for circulation, silver must always retain a worth among men that will bear a steady relation to the necessities of life.

On the other hand, the political economist recognises in gold a substance depending in value upon more fortuitous circumstances. Existing in commerce in *quantities* estimated by some authorities as 50 times less than that of silver, or where reckoned with reference to *value*, 3 times less, it must, more than the former metal, partake of the mobility of a smaller body. Its demand for articles of ornament makes it somewhat subject to the caprices of fashion, and more important than all, as a substance occurring in nature close to the surface, in deposits worked generally with little exercise of skill, and readily exhausted, and being a metal that requires but little preparation after leaving the hands of the miner to make it ready for the market, gold wants those elements of stability, and those essential connections with the cost of labour, which would recommend its choice as a standard of value.

It is an interesting task to study the variations in the relative value of gold and silver within the past three centuries. At the date of the discovery of America,

Spanish law made $11\frac{6}{10}$ parts of silver equivalent in exchange to 1 part of gold. When the stream of silver, poured into Spain from the mines of Pasco, Potosi, and Zacatecas, began to re-act upon European markets, the relative value of gold rose, so that even in the first century after the discovery of America, 12 parts of silver were exchanged for 1 of gold. Since that date, influenced by variations in supply and demand, 12 and even 17 parts of silver have been considered in the market equal to 1 part of gold. In 1837, one pound of gold would buy in London $15\frac{6.5}{100}$ pounds of silver; and in France a law is in existence fixing the worth of gold at $15\frac{5}{10}$ times that of silver.

CHAPTER II.

HISTORICAL SKETCH OF LEAD.

IN ancient times lead appears to have held quite a subordinate position among the metals, both as regards the number of its uses and the value it possessed in the market. Of its discovery history furnishes us with no information. The Greek term *molybdus*, by which the metal was known, is so closely analogous to its Indian name, *mulva*, that some authors have been led to the conclusion that the knowledge and usage of the metal originated in remote ages in the distant East, and from hence was disseminated among the nations of Europe.

Nature produces, in sufficient quantities to attract the attention of the primitive worker in metals, only

such compounds of lead as furnish the pure metal after a chemical process requiring the aid of heat; so that, unlike gold, copper, or silver, its earliest use must have come subsequent to that condition of cultivation that enabled the reduction of an ore. The discovery of native lead among natural productions is due to the scientific acumen of more recent times.

An elementary acquaintance with the properties of ores once possessed, it is not difficult to follow the course of reasoning and experiment that would lead to the discovery of lead. Its most valuable and abundant ore—galena—possesses so many qualities calculated to make it remarked by an uncultivated race; its weight, its brilliant metallic glance, its hardness, would all favour the conclusion that it was an unrefined metal, and a very simple operation of the mind would lead to the attempt to make it malleable by subjecting it to the action of the fire. The occurrence of the ores of lead with silver, and the attempts to purify the latter, may have been the immediate cause of the discovery of the former metal.

The winning of lead from plumbiferous silver ores was in the earliest times not connected with the reduction of the litharge, as is at present so generally the case. The lead was deemed the impurity of the more precious metal, and was “burned” or oxidised away, as has been described in the history of silver.

The earliest mention that we have of lead occurs in Numbers, where it is spoken of with various other metals among the spoils brought by the children of Israel to Moses, after their victories over the Midianites; and it is evident that the same metal was an

article of trade, together with silver, iron, and tin, at the fairs of the Phœnicians.*

The Romans employed for lead the name *plumbum*, which clearly had its origin in the Greek and Indian appellations. They appear to have regarded lead and tin as but varieties of the same metal, distinguishing the former as black lead, and the latter as white lead. Remarkable differences, however, were observed as existing between the two, and the process of collecting the mineral, producing the white variety (stream tin) from the *débris* of the valleys, is distinctly described; and, further, the fact that *black* lead only, of the two varieties, could be refined for the purpose of obtaining silver, appears to have been well understood.

The employment of lead in ancient times was much less general than one might anticipate from the abundance with which it occurs in nature. It was often used in connection with tin as an alloy, and this mixture, being employed in the manufacture of bronze, probably led to the introduction of the lead which is found to constitute a portion of many works of plastic art, and coins, that have descended to us. I have seen, in the Museo Borbonico, at Naples, portions of an ancient water conduit from the island of Capri, in which an exceedingly malleable lead was employed apparently for tightening the joints. Lead also appears to have been made into plates and tubes, and to have answered as a material for vessels for household purposes.

Some of the chemical compounds of the metal appear to have been well known to the Romans. Litharge, produced in the treatment of argentiferous lead, was a common substance. As it was crystalline or amor-

* Ezek. xxvii. 12.

phous, or more or less pure, it received different names, which names were supposed to designate entirely different substances. The finer qualities were employed in medicine, in the preparation of plasters.

What is now known as white lead was called by the Romans "*cerussa*," and they prepared it by a method not very dissimilar to that in use at present in many localities, by allowing vinegar to act upon the commercial metal. This substance was used as a colour, and also extensively in medicine. It is related that some casks of white lead, that happened to be in a burning building, were so affected by the heat, that their contents became a fine red colour that was found to make an excellent pigment, and which, after this accidental discovery, was manufactured and sold under the name of "burned white lead." This was the beginning of the knowledge of what we call "red lead," a substance now so valuable to the painter. The Romans knew how to reduce the litharge formed in the process of smelting silver to the condition of metallic lead, but this knowledge, limited as it may seem, does not appear to have been possessed by the tribes of eastern Siberia, where Gmelin states that he observed the remains of many old furnaces where silver had been extracted, but where the lead with which it had been combined was, after oxidation, thrown away.

The poisonous qualities of the vapours of lead were known to the ancients, and the deplorable effects it produces upon labourers employed in the furnace were early noticed, as were also the highly poisonous qualities of many of the lead compounds. Although they appear to have used lead in the form of a thin

sheet, to detect by its colour, upon being immersed in wine, the state of acidity to which that fluid had arrived, it does not appear that they had discovered the more modern plan of adding litharge to sour wine, for the purpose of improving its taste, by bringing about therein the formation of a sweet salt.

The countries standing first as producers of lead in modern times are Great Britain, Spain, and the United States.

The royal decree that in 1825 opened the Spanish mines to native and foreign competition was followed by a period of rapid expansion in the mining and metallurgic industry of the kingdom. For a period previous to 1820, with the exception of a few inconspicuous iron pits, the only mine in activity in Spain was that of Almaden, where the Government monopolised the production of quicksilver. But in 1826 no less than 3000 mines had been opened in the Sierras of Gador Lujar. So large and rich were the lead deposits here, that in 1823 the production of the region had reached 25,000 tons per annum, and in 1827 the quantity produced was 42,000 tons. The markets of the world were soon overflowing, and, as a consequence, a universal depression in the price of lead was experienced throughout Europe, and many of the poorer mines of Germany and England were compelled to suspend operations. At length, in order to raise the price of the metal to a remunerative point, the miners of the country were obliged to enter into a mutual agreement to work the deposits only during half the year.

These vast stores of metal were, however, chiefly near the surface; their productiveness soon began to diminish. Their point of culmination was in 1827, since which there

has been a rapid falling off, until at present the yield is comparatively inconsiderable.

The lead and silver mines of Sierra de Almagrera were discovered in 1839, and the excitement which the discoveries there made produced was extraordinary. The influx of population was such that in 1845 8000 miners were employed in that district in 826 mines, and there were 38 smelting works in operation, which produced in that year 108,230 pounds troy of silver and 8350 tons of lead. The ore which furnished the great quantity of precious metal was an argentiferous galena holding from 130 to 180 ounces of silver to the ton. But upon sinking deeper the miners found that their ore decreased in quantity, and this deposit has also become of less importance than it formerly was. Besides these districts, the ancient mining region of Linares has produced much lead since having become a locality for the exertion of English enterprise.

Great Britain contains a large number of lead-bearing districts, and her production of this metal, as well as that of tin, copper, and iron, exceeds that of any other land. The production of silver and lead are intimately connected, and the introduction of new processes that will be described in subsequent chapters, has brought her yield of the latter metal to a large figure during the last few years.

From the circumstance that pigs of lead, evidently of Roman origin, have been found in Derbyshire, we are led to the conclusion that Britain was a lead-producing country even in those remote times. It is generally stated that Derbyshire supplied the only mines where that metal was raised until 1289, when the lead deposits of Wales were discovered. In 1661

Childrey, speaking of the Peak of Derbyshire, gives the following curious account of the treatment of the ores in that district :—" The lead stores of the Peak are just within the ground, next to the upper crust of the earth. They melt the lead on the tops of the hills that lie open to the west wind, making their fire to melt it as soon as the west wind begins to blow, which wind, by long experience, they find holds longest of all others. But for what reason I know not, since I should think that lead was the easiest of all metals to melt, they make the fires extraordinarily great."

The most important lead-mining district at present is in the north of England, in the vicinity of Alston Moor, where the three counties of Northumberland, Durham, and Cumberland come together. Near this point are the large possessions of Mr. Beaumont, which produce about one-fourth of the whole quantity of lead raised in England, and one-tenth of the entire yield of Europe.

The increase in the amount of lead raised in Cornwall and Devon within the last twenty years has been quite extraordinary. Borlase, who wrote in 1758, says, that lead mines had been anciently worked in the first-named county; that those of Penrose, near Helston, had been wrought for about 200 years, but the only mine worthy of note in his time was that of St. Issy, near Padstow. In 1835 only about 140 tons were produced by the mines of the two counties, and in 1839, according to De la Bèche, the whole produce amounted to scarcely 180 tons, while in the years from 1845 to 1850 over 10,000 tons were raised annually. One mine alone of extraordinary richness, East Wheal Rose, produced from 1845 to 1849 from 3000 to 5000 tons of metallic lead

annually. In 1858, 9710 tons were sent to market from 34 Cornish mines, and among these were 13, each of which furnished more lead than was raised in the whole county twenty years before.

The ore raised in Cornwall is largely silver-holding; the average of that metal per ton of lead produced in 1858 was 41 ounces, while the average for the entire United Kingdom for the same year was between 8 and 9 ounces. Isolated mines produce ore much richer than the above average; thus Huel Mary Anne in 1858 yielded 906 tons of lead, containing an average of over 68 ounces. The mines of Derbyshire furnish some examples of ores extremely rich in silver. Huel Florence gave ore in 1858 containing 150 ounces, or equivalent to 225 ounces per ton of metallic lead. Two tons of this ore realised 193*l.* 16*s.*

The yield of the lead mines of Great Britain in 1810, although exceeding in amount that of all the rest of Europe, did not amount to over 12,500 tons. In 1845, according to the estimates of Mr. Taylor, it had increased to 46,112 tons. In 1858 the invaluable statistics prepared by Mr. Hunt show that 68,303 tons of metallic lead were produced from 95,855 tons of ore, being an average of 71 per cent.

There are few articles occupying such an important place in commerce, that experience such large variations in price, as lead. In the period between 1800 and 1810 its average price was 27*l.* 14*s.* 6*d.* per ton; from 1811 to 1821, 23*l.* 6*s.* 6*d.*; from 1822 to 1832, 20*l.* 7*s.* In 1832 the price was as low as 13*l.* 10*s.*, and in 1858 the mean value per ton was about 21*l.* 10*s.*

In the United States, in relation to the value pro-

duced, lead stands immediately after gold, iron, and copper. Its ores are widely distributed among the several States, but by far the most considerable amount is raised in that portion of Wisconsin, Iowa, and Illinois, which is generally known as the "Upper Mississippi Lead Region." Here the ore is a non-argentiferous galena, occurring in limestone in irregular deposits or veins that do not appear to retain their richness below a moderate depth. The ancient inhabitants of the country appear to have been aware of the existence of the mineral, but it is doubtful whether they understood the process of smelting it, for although galena has been found in their sepulchral mounds, no metallic lead has as yet been discovered. Le Sueur, the French explorer, notices many mines of lead along the bank of the Mississippi during his expedition in 1700-1701, but little attention appears to have been paid to the wealth there until, in 1788, a French miner named Dubuque obtained a grant of a tract of land and opened mines, which he continued to work until his death in 1810. In 1839 a geological exploration was ordered by the United States Government, and, aided by 139 assistants, Dr. D. D. Owen made a rapid exploration of a region embracing 2880 square miles, which he reported to be plumbiferous.

The lead deposits of the Mississippi, geologically, have many points of resemblance to those of Andalusia, and, like them, they appear to have reached their maximum production but a brief period after vigorous working commenced. The investigations of Whitney have shown that the production of the region is declining rapidly. In 1845 the mines of the Upper Mississippi reached their highest yield with 24,328 tons; in 1853 this had sunk to 13,300

tons. The market of the world is but little influenced by these mines; they being scarcely sufficient to supply the immense demand for lead in the valley of the Mississippi.

CHAPTER III.

THE PHYSICAL AND CHEMICAL PROPERTIES, AND SOME OF THE MOST IMPORTANT ARTIFICIAL COMPOUNDS OF SILVER.

SILVER exceeds all other metals in whiteness, and it may be made, by careful polishing, to receive a lustre almost equal to that of burnished steel. It crystallises in octohedrons and cubes. If a sufficiently large quantity of pure metal be fused in a crucible and allowed to cool very slowly until partly solidified, then, after piercing the crust and pouring off the still fluid interior, the walls of the cavity will often be found coated with beautiful octohedral or cubic crystals. The precipitation of silver from solution by means of a weak electric current, is often attended with the formation of distinct crystals.

Its specific gravity or weight compared with an equal bulk of water, varies slightly according to the treatment it has previously received; thus—

When cast, it is 10·474.

When hammered, 10·542.

It will be seen that silver follows closely after lead in regard to weight, exceeds copper, iron, tin, and zinc; and that it has almost exactly half the specific gravity possessed by platinum. It is inferior to gold in its capacity to be hammered into thin leaves, but

exceeds all other metals. It requires to be annealed oftener than gold in the process of hammering, that it may retain its malleability. It is extremely tenacious, and may be drawn into wires, only exceeded in tenuity by those of gold, it being possible to draw a grain into a wire 400 feet long. It is the fourth metal in the order of tenacity, following iron, copper, and platinum; a wire 0·787 lines in diameter will sustain 184·14 pounds. It is harder than gold, and only a little softer than copper. In forming an idea of this property, the reader must be careful not to be led into error by observing the coins in common circulation. These are much harder than the pure metal, being purposely made so by alloying them with a small portion of copper. Silver has no effect upon the organs of taste or smell; it is particularly sonorous, and gives a clear, pleasant ring when struck. In its power to conduct heat, it takes a medium position between gold and copper; its lineal expansion when heated from 32° to 212° is about $\frac{1}{500}$, and it ranks with copper above the other metals in its capacity for conducting electricity.

According to the determinations of Daniell, silver fuses at 1873° of the Fahrenheit, and 1023° of the Centigrade thermometer, and at 22° of the Pyrometer of Wedgwood; hence, it becomes liquid at a temperature inferior to that necessary to fuse gold and copper. At the temperature of common furnaces, silver is but slightly volatile, when exposed to the heat of a porcelain furnace it lost 0·005, or less than copper; but when subjected to the action of an oxyhydrogen blowpipe, or placed in the focus of a powerful lens, it evaporates rapidly, gives off a green light, and the vapours take fire.

A singular phenomenon is often to be observed when pure silver is fused in the air and cooled rapidly. Upon the exterior of the mass becoming hardened, the interior seems to expand, and, fracturing the thin crust, sends out sprouts of what appear to be a species of metallic vegetation. A purely physical explanation was formerly given for this appearance. It was assumed that the interior fluid, in the moment of hardening, as is the case with bismuth, experienced a sudden expansion that served to break the crust and eject a portion of the liquid.

Gay-Lussac, who studied the subject with care, found that in the moment of hardening after having been fused in the air, silver gave out oxygen gas to the amount of at least twenty times its volume, and that it was the sudden liberation of this gas that broke the crust and projected the metal through the apertures. Loss is not unfrequently experienced by particles of silver being thrown into the air, but this may be prevented by allowing the mass to cool very slowly, so that the interior may become solid almost at the same moment with the exterior; and thus, by permitting the confined oxygen to go off through fluid metal, an explosion will not ensue.

Plattner, who investigated this subject, concluded, in opposition to most chemists, that, like copper, silver was capable, while in a fluid condition, of absorbing a large quantity of its compound with oxygen; and that at a reduced temperature this compound could not exist, but at the moment of cooling became suddenly decomposed, and its gas set free.* If silver be run into small bars, so that its surface is cooled rapidly, a

* Plattner's Metallurgischen Röstprozesse, p. 123.

portion of the interior retains this oxide mixed with the metal, and hence follows the brittleness resembling that of "dry copper,"* which is often observed in small silver ingots.

SILVER CHEMICALLY CONSIDERED.

The chemical symbol of silver is Ag from the Latin *Argentum*. The proportion with which it combines with other substances indicates that its atomic equivalent in the hydrogen scale is 108, and in the oxygen scale 1349.01.

Perfectly pure silver may be obtained by employing the following method:—The commercial metal should be dissolved in slightly diluted nitric acid, and a solution of chloride of sodium, or common salt added. This precipitates the chloride of silver, while the salts of the adulterating metals remain in solution. The precipitate is now thrown upon a filter, thoroughly washed and dried. A quantity of carbonate of potash, equal to twice the weight of the chloride of silver is fused in a crucible, and the dry chloride gradually added to it, whereupon the chloride of potassium is formed, and carbonic acid and oxygen escape with effervescence. The crucible is exposed to a heat sufficient to reduce the silver which subsides to the bottom, and will be found entirely pure.

The silver of commerce has generally an intermixture of a small quantity of lead, and sometimes copper, gold, antimony, and arsenic. The silver manufactured from some ores always contains gold; and instances have occurred in Germany where the owners of metallurgic establishments, for the want of a proper chemical

* See Rudimentary Treatise on the Metallurgy of Copper, page 144.

investigation, have for a long time thrown into market an auriferous metal that would have paid largely for the parting.

In the air, and at common temperatures, silver does not tarnish; but it is so sensible to the action of sulphuretted hydrogen, that where the least trace of that gas is present it at once attacks the silver, producing a dark sulphide. This phenomenon is often observed in daily life; the silver spoons placed in food containing sulphuretted hydrogen—as, for instance, cooked eggs—become disagreeably blackened. In order to clean objects that have been thus attacked, the most simple means is to plunge them for a few minutes in a solution of the manganate of potash, or *cameleon mineral*. In water silver is not changed, and only a few acids will dissolve it.

Nitric acid is the proper solvent of silver; it yields to this fluid even in the cold with the production of the nitrate of silver and the disengagement of deutoxide of nitrogen.

Sulphuric acid in a dilute condition does not attack silver, but when hot and concentrated it dissolves it, at the same time setting free sulphurous acid. Upon this circumstance rests one of the most advantageous methods of separating silver from gold, upon which latter metal sulphuric acid has no effect.

Hydrochloric acid attacks silver sensibly, particularly when in contact with platinum. *Aqua regia* changes it rapidly to a chloride, and a coating of the same compound is formed when silver is kept for some time in contact with fused common salt.

With the exception of gold, silver resists more perfectly than any other metal the action of *nitre* and the

caustic alkalies; hence, in fusing substances in contact with these compounds, crucibles made of silver instead of platinum should be used.

Upon silver, *vegetable acids* produce no effect, and hence its superiority as a substance for forming culinary utensils.

COMBINATION OF SILVER WITH OXYGEN.

Three oxides of silver are known to chemists; the suboxide, Ag_2O ; the protoxide, AgO ; and the peroxide, AgO_2 .

The *suboxide* is a rare substance formed by passing a current of hydrogen over a citrate of silver; it is very unstable, being readily decomposed by a slight heat into silver and oxygen.

The *protoxide* (AgO) is far the most important of the three compounds. It consists of

93.06 parts of silver,
and 6.91 ,, ,, oxygen.

When a solution of the nitrate of silver is treated with an excess of potash, this oxide falls as an olive grey powder, which grows darker by drying. It is a strong base, forming neutral salts with the most powerful acids, but is readily decomposed by heat into its constituent elements, and it also suffers decomposition when exposed to the light. Treated with caustic ammonia, the oxide of silver forms a dangerously explosive compound, which is prepared as follows:—The oxide of silver precipitated from a solution of the nitrate is thrown upon a filter, and allowed to drain. Caustic ammonia is now poured upon the still moist oxide, and the two bodies are left in contact during several hours. The liquor is then

decanted, and the black powder that remains removed in small quantities, and with precaution, to a piece of soft grey paper. Too much care cannot be exercised by those experimenting with this substance, since it detonates with great violence when rubbed with a hard body even when immersed in water.

The *peroxide* (AgO_2) of silver is formed by decomposing a dilute solution of the nitrate by means of a current of galvanic electricity. Up to the present time it does not appear to have been produced in a pure condition.

Silver may be made to form a compound with carbon by fusing it with that substance in an earthen crucible. The carbon thus taken up will be deposited as a black flocculent mass when the metal is dissolved in dilute nitric acid.

THE SALTS OF SILVER.

The protoxide of silver forms salts with various acids. Colourless acids produce colourless salts, but when these are exposed to the light of the sun they are partly decomposed, and become darkened. When in solution they may be recognised by the following reactions:—

1. *By giving a white curdy precipitate with all soluble chlorides.* This is the most commonly employed, and the best test for silver, and is the reaction by means of which it is separated from other metals. The solubility of this precipitate in ammonia, and its insolubility in acids, makes it difficult to mistake it for that of any other mineral. It is also extremely delicate, the experiments of Malaguti and Durocher having shown that when water contains but $\frac{1}{40000}$ of a silver

salt, that the addition of a little chloride of sodium will produce a distinct opalescence.

2. *By giving with sulphuretted hydrogen a black precipitate.*

3. *By the white precipitate of carbonate of silver, which falls when a little carbonate of ammonia is added, and which is soluble in a larger quantity of the reagent.*

4. *By chromate of potash, which forms a reddish brown precipitate, readily soluble in water.*

5. *Before the blowpipe the salts of silver are promptly reduced when heated on coal with a small quantity of soda.*

Chloride of Silver.

This substance is a natural production common in some mines. It is also frequently formed in the laboratory by precipitating a soluble salt of silver by means of a chloride. When the sulphurous ores of silver are roasted with the access of air and the addition of a certain quantity of common salt, the silver that they contain is transformed into a chloride.

This compound plays an important part in the treatment of the ores of silver upon a large scale. Both the European and American systems of amalgamation require that a great part of the silver shall pass through the intermediary condition of a chloride before being taken up by the quicksilver. The method of Patera in use in Bohemia is founded upon the solubility of this compound in hyposulphite of soda, and that of Agustine, which is in use at Freiberg, in Saxony, takes advantage of its solubility in a hot solution of common salt. The amount that a solution of chloride of sodium will take up depends on the

temperature of the solution. At 32° an almost insensible quantity is dissolved; at 50° , 0.0017 of the weight of the common salt present will be taken up; at 64° the capacity has increased to 0.0024, and toward 212° to 0.0068 of the amount of salt in the brine. Chloride of silver is soluble, when recently precipitated, in the sulphites as well as the hyposulphites of potash and soda, producing double salts; and also in ammonia and the hot solutions of the chlorides of potassium, sodium, barium, strontium, and calcium. It is, however, completely insoluble in pure water.

Fluorine, cyanogen, bromine, and iodine combine, like chlorine, directly with silver; and the two last-named elements produce substances found in nature, to which reference will be made in the chapter treating of the minerals of silver.

It is upon the sensitiveness of these compounds to light that the daguerreotype and calotype processes owe the accuracy and beauty of their results.

Sulphide of Silver.

It is probable that silver exists in this form in nature, more abundantly than in any other. It is found massive or crystallised in cubes or octohedrons, and is so soft that it may be readily scratched with the nail, and so malleable that medals have been struck from it.

Nitrate of Silver.

This is the best known of all the salts of silver, being familiar to most persons in its solid form as *lunar caustic*, which is usually sold in slender sticks that

Sulphuret

have been formed by fusing it and casting it into moulds. It is not less familiar in solution as *indelible ink*, which is much used for marking linen. When pure the salt consists of

$$\begin{array}{r} 68\cdot22 \text{ parts of oxide of silver,} \\ \text{and } 31\cdot78 \text{ parts of nitric acid.} \\ \hline 100\cdot00 \end{array}$$

It crystallises in beautiful hexagonal tables, which are colourless and unalterable in the air; but *lunar caustic* has usually a colour more or less dark, caused by the reduction of a small quantity of the salt, and the formation of finely divided metallic silver, during the course of its preparation for market, or by subsequent contact with some organic body.

When the solution is used for writing on linen, it is by a similar formation of metallic silver that the black marks are produced. It may be useful for those who are in the habit of using this ink to remember that the dark violet spot which is produced when a drop falls upon the skin, may be removed by rubbing it with the iodide of potassium, or the bichloride of mercury.*

Fulminate of Silver.

This salt corresponds to a dicyanide, and contains 77·32 parts of the oxide of silver. It is readily made by dissolving a small quantity of silver in nitric acid, adding alcohol, and heating. When a precipitate begins to fall the vessel must be removed from the fire, and more alcohol added. The precipitate, which is the

* In cases of poisoning by nitrate of silver, an emetic should first be administered, after which a strong dose of salt water should be given.

fulminate, gradually collects at the bottom, and may be thrown upon a paper filter and carefully washed and dried, when it is ready for use. The utmost care must be exercised in handling this dangerous compound, and only a small quantity should be dried at once. An instance is on record where an unfortunate chemist was torn to pieces by the explosion of about a pound, which he had been engaged in preparing. It is occasionally employed in the arts in common with the fulminate of mercury for filling percussion caps.

Sulphate of Silver.

When silver is dissolved in hot sulphuric acid, this salt is produced: it is tolerably soluble in that fluid, though but slightly so in water. In the separation of silver from gold on a large scale, this salt is formed, but is usually subsequently reduced to a metallic state.

CHAPTER IV.

THE PHYSICAL AND CHEMICAL PROPERTIES, AND SOME OF THE MOST IMPORTANT ARTIFICIAL COMPOUNDS OF LEAD.

LEAD has a bluish grey colour, and, when its surface is freshly cut, possesses much lustre. When cooled slowly it crystallises in small octohedrons. It is the softest of the common metals, and, when pure, may be scratched by the nail, or used like graphite for writing upon paper. It occupies the 7th place among the metals in regard to malleability, being less disposed to break in pieces beneath the hammer than iron or zinc, but its malleability is exceeded by silver,

copper, and tin. As regards ductility, it stands among the lowest, since it can be drawn into wire with less facility than zinc or tin. Its tenacity is also extremely low, a wire, .787 lines in diameter will sustain but 27.621 pounds, or less than $\frac{1}{20}$ as much as an iron wire of the same size. It is very inelastic, and gives a dull sound when struck. Some of its alloys are, however, sonorous, since a favourite composition for organ pipes consists of about 50 per cent. each of tin and lead, which is brought to its required form by casting, thus producing a crystalline structure which is necessary for securing the finest tones.

The determination of the specific gravity of lead has given occasion to many careful and often-repeated experiments. Such is the largeness of its relative weight, that nearly all substances that can form a disadvantageous mixture with it are so much lighter, that their presence, even in a small proportion can be detected by a determination of its specific gravity. Hence the excellence of a commercial article can often be judged by knowing its weight when compared with water. In consequence of this fact, large lead consumers sometimes set a certain specific gravity, which all lead sent to them for sale must attain.

Berzelius gave the specific gravity at 11.445, and this number is to be found in most works in which the subject is mentioned; but recent experiments show that it is entirely too high. Professor Reich has given the subject a careful investigation within the past year, and his results indicate that the specific gravity of pure lead is not over 11.370, when its temperature is 32°, and when compared with water at its greatest density.

The intimate connection which exists between the specific gravity of lead, and its excellence when considered as a commercial article, is well illustrated by the following table, which has been selected from the valuable determinations of the gentleman just named.

It will be observed that the second column contains the specific gravity of the metal, after which follow the amount of lead, and impurity, for each sort as shown by chemical analysis.

SORT OF LEAD.	Unreduced Specific gravity.	Per Cent. of						
		Lead.	Copper.	Iron.	Nickel.	Antimony.	Arsenic.	Sulphur.
Very impure lead . . .	10·787	92·41	0·18	0·04	tr.	5·54	1·64	0·13
The same after 6 hours' refining }	10·987	undetermined.		0·016	0·08	undetermined.		
The same after 14 hours' refining }	11·162	97·56	0·44	0·03	0·03	0·74	0·56	—
The same after 19 hours' refining }	11·340	98·68	0·54	0·03	0·04	0·06	0·05	—
The same after being submitted to Pattinson's process }	11·373	undetd	0·095	0·06	—	0·01	0·01	—
Rich lead from Pattinson's process with 0·628 per cent. silver }	11·347	„	0·05	0·03	—	0·03	—	—
Assayer's lead after having passed through Pattinson's process ; free from silver . . }	11·381	„	0·07	0·06	00	00	00	
Hard lead	10·403	91·80	0·69	0·12	—	3·98	3·24	

Not only does the specific gravity of lead decrease as it becomes impure, but, unlike other metals, a similar physical change has been observed by some experi-

menters to take place when it is subjected to the processes of hammering or drawing into wire. Professor Reich, who has also made a number of experiments upon this subject, found that pig lead at 11.352 specific gravity remained almost without change when rolled to a plate half an inch thick. This paradoxical result is probably owing to the interior of the metal assuming a laminated condition.

Lead transmits heat very slowly, being, among the seven common metals, the worst conductor. Its point of fusion is comparatively low, being but about 612° of the Fahrenheit scale. Bismuth and tin melt more readily, but zinc yields to the fire with less ease.

LEAD CHEMICALLY CONSIDERED.

The atomic weight of lead is 103.5 by the hydrogen scale, and 1294.5 when oxygen is assumed as 100. Its chemical symbol is Pb, from the Latin *plumbum*, and by the alchemists it was named *Saturn*, and was designated by the sign P .

Exposed to the action of moist air, lead becomes covered with a dark coating, which has been shown to be the protoxide; the action continuing, carbonic acid is absorbed from the air, and the white carbonate is produced. Distilled water, from its affinity for the oxide of lead, determines the oxidation of that metal; in the presence of the air this is gradually changed to the white hydrated carbonate, which frequently forms distinct scales upon the surface of the metal. In such cases the water is invariably found to hold a portion of lead in solution, which is readily proven by its becoming brown on passing through it a current of sulphuretted

hydrogen gas. The presence of a very small quantity of a foreign salt in the water, and particularly the sulphate of lime, has the property of almost entirely preventing the oxidation and solution of the lead; and since river and spring water is always more or less impure, its action upon leaden pipes or reservoirs is generally slight. But since the carbonate of lead is an energetic poison, it is unsafe to use water-pipes of lead until it has been proved by experiment that the particular water in question does not act upon this metal.

In buildings where lead is placed in contact with wood undergoing rapid decay, it is destroyed in a short time, under the simultaneous action of the acetic acid produced by the decomposition of the wood, the carbonic acid of the air, and water. Direct experiment has proven, that lead placed in contact, or even at a small distance from rotting wood, quickly loses its tenacity, and is transformed into a mixture of the acetate and carbonate, while zinc in the same position only experiences a superficial oxidation.

Heated to fusion in the air, lead is first covered with a play of iridescent colours, resulting from the formation of a thin pellicle of the oxide. This is soon supplanted by a yellow scum of the same substance, and if it is desired to continue the oxidation, this must be taken away, in order to expose a fresh surface. When the temperature is carried to redness, the metal gives off distinct vapours, which burn in the air with a white livid flame.

Some of the lead in commerce is extremely pure, that of England having long held a very high place in this respect. The following analyses will show

(in connection with those already given, p. 37) the amount and nature of the impurities generally met with :—

	Lead.	Copper.	Silver.	Anti- mony.	Ar- senic	Zinc
From the Upper Hartz . {	97·65 to 98·51	0·06 to 0·14	— —	1·00 to 1·34	0·36	0·88
Spanish lead	99·84	0·13	0·0038	0·03		
English lead	99·75	0·20	0·0060	0·05		
Nassau lead	98·63	1·64	—	—	—	—

Where lead of still greater purity is required, it may be procured by reducing, in a lined crucible, oxide of lead obtained by the decomposition of crystallised nitrate of lead.

The proper solvent for lead is *nitric acid*, which will attack it even in the cold, oxidising it rapidly, and forming with its oxide a salt, readily crystallising on cooling in opaque octohedrons.

Sulphuric acid, if weak, and the air be excluded, does not act on lead, but when hot and concentrated acid is used, a sulphate is formed, and sulphurous acid given off.

Hydrochloric acid does not act upon it sensibly, but *aqua regia* converts it into a chloride.

Combinations of Lead with Oxygen.

Lead combines in three proportions with oxygen, as follows :—

Suboxide	Pb_2O ,
Protoxide	PbO ,
Peroxide	PbO_2 .

The second and third of these compounds combine with each other, giving intermediary compounds known as miniums.

The *suboxide* (Pb_2O) is produced in the laboratory by heating the acetate of lead to about 600° . This is a dark substance, which, when heated in contact with the air, goes over into a protoxide.

The *protoxide of lead* (PO), which is otherwise known as *massicot*, or *litharge*, is composed, when pure, of—

$$\begin{array}{r} 92\cdot83 \text{ parts of lead,} \\ \text{and } 7\cdot17 \text{ parts of oxygen.} \\ \hline 100\cdot00 \end{array}$$

This is one of the commonest of the compounds of lead; it was an article of commerce even among the ancient Romans. Its colour varies between a yellowish citron and a yellowish red, the latter varieties always containing—according to some chemists—a mixture of a certain quantity of minium, or red lead. It enters into fusion at—according to Plattner— 1749° Fahr., which is considerably above the melting point of lead, but below a red heat; upon cooling, it crystallises in thin micaceous plates. In pure water it dissolves to the amount of $\frac{1}{7000}$ th, but this solution does not take place when the water has salts, such as the sulphate of lime, already in solution. When fused in contact with the atmosphere, it absorbs oxygen like silver (p. 27), and gives off this gas again upon cooling; and when heated to about 600° in a current of air, it absorbs oxygen and is transformed into minium. With energetic bases it combines, playing the part of an acid, and sometimes forming crystallisable salts. The compound with lime is occasionally used as a hair-dye, the

sulphur which forms a portion of the organic substance re-acting upon the lead, and producing the black sulphide which serves as the colouring matter.

Protoxide of lead may be formed in a variety of ways; the most usual of which is to expose the metal in a fluid condition to the action of the air. Thus the litharge of commerce is obtained, being a product in the process of cupelling of rich or argentiferous leads. The red variety brings the best price, and is hence most usual in the market, where it bears the reputation of always being purer than the yellow. The latter, however, may be given a red tinge by bringing it to the condition of a powder, and heating it in a reverberatory furnace in contact with the air. By varying the method of preparing it, the chemist is able to obtain this oxide with a great number of tints, from colourless through all the degrees of yellow into yellowish brown.

The use of the oxide of lead in the arts is quite extensive. It furnishes the assayer with a valuable flux, which, if necessary, can be replaced by carbonate of lead. It forms a very fusible compound with the alkalies, but the earths require a considerable excess when it is required to bring them to the state of fusion. With the larger number of metallic oxides, it readily enters into combination, and it fuses and combines with silica and the silicates. Employed in a large excess it decomposes all the sulphides, most frequently in oxidising both elements; but when the proportion of litharge is not sufficient to produce this effect, one portion of the sulphide is decomposed, and the other portion combines with a portion of the litharge which is not reduced, and with the metallic oxide that has been formed.

The fact that litharge has the property of oxidising most of the metals except silver, gold, platinum, and mercury, and forming fusible compounds with these oxides, gives it the great value which it possesses in the purification of these metals upon a large scale, as well as in the laboratory of the assayer.

The *peroxide of lead* (PbO_2) is brown, or nearly black, insoluble in water, and decomposable below a red heat, passing into minium. When mixed with a small quantity of sulphur, it produces a powder that may be inflamed by rubbing. The peroxide of lead may be formed from minium by treating it with nitric acid.

MINIUMS.

The compounds formed by the combination of the peroxide of lead with the protoxide have received the general name of miniums, and are known in commerce as red lead. They have a composition that in general may be expressed by the formula Pb_3O_4 ; but several other proportions of the two elements are recognised by chemists. Red lead being the object of manufacture on a large scale, it will be mentioned more particularly in another place. It is chiefly employed as a paint, also for colouring paper and sealing-wax, and in the manufacture of glass.

SALTS OF LEAD.

The protoxide of lead forms numerous salts, which are uncoloured when the acid which forms a portion of the combination is uncoloured. Their taste is usually

sweet or styptic, and the soluble salts of lead are active poisons.*

The soluble salts of lead may be recognised :—

1. *By giving a black precipitate with sulphuretted hydrogen, which, when much hydrochloric acid is present, is brown or red.*

2. *By giving a white precipitate with sulphuric acid,*

* Of all cases of poisoning by metallic compounds that are brought to the notice of physicians, those produced by the salts of lead are the most frequent. All classes of persons whose business brings them in frequent contact with the metal, in any of its forms, are subject to it. Among these may be mentioned the manufacturers of white and red lead, smelters of lead ore, grinders of colours, type founders, and potters, and less frequently, manufacturers of glazed cards, printers, glass makers and tinmen. The poison may be introduced into the body in two ways :— by breathing it in the form of fumes, and thus taking it into the lungs ; and by swallowing it. By the former manner it is introduced into the system of those who sleep in freshly painted rooms, or are employed in furnaces where lead is fused. Numerous cases of poisoning have occurred in the second manner by drinking water which has passed through leaden conductors, by eating candies coloured with lead, or drinking wine and cider *improved* by litharge. It is still a question whether lead can be introduced into the system by handling its poisonous compounds. After a long exposure to the fumes of lead, the body becomes so charged with the metal, that if a sulphurous bath be applied, many parts, and particularly those beneath the nails, become quite darkened by the black sulphide. The disease may not follow until after the several months or even years of exposure, when it suddenly sets in, and cases are on record in which the patient had not been exposed to the action of the poison for several months previous to his attack.

The symptoms are ordinarily a violent pain in the bowels, which occurs at intervals, and which the patient seeks to assuage by pressure, it being a peculiarity of the disease that it may sometimes be made less painful by applying a flat body like the palm of the hand forcibly to the affected part. Occasionally the pains extend to the limbs and muscles, and after several attacks, the disease may end in paralysis and death. Another species of the same affection terminates in delirium, occasionally attended by the wildest frenzy, or the sufferer's life terminates with violent convulsions.

The remedies recommended by physicians for the painters' colic, are numerous, and more or less efficacious. The milder cases may be treated with sulphurous waters and sulphuric acid in a very dilute condition, but

or the soluble sulphates, which, upon the addition of sulphuretted hydrogen, grows dark.

3. *By giving with carbonates of potash and soda the white carbonate of lead, which is insoluble in an excess of the precipitant.*

4. *When heated before the blow-pipe on coal with soda, the salts of lead are reduced to metallic lead, and the coal is covered with a yellow coating of oxide.*

Chloride of lead (PbCl) is a white, slightly soluble substance, which may be formed by the direct action of chlorine gas upon lead when heated to redness, or by dissolving the oxide in hot hydrochloric acid.

The *oxychlorides of lead* exist in nature in two forms. In the arts the chemical compound, having the formula $\text{PbCl}, 7\text{PbO}$, is known as yellow mineral, Paris yellow, or Turner's yellow. The manufacture of this substance will be spoken of in a subsequent chapter. The chloride and oxide of lead appear to unite, when fused together, in all proportions.

SULPHIDE OF LEAD, OR GALENA.

This compound is the most abundant ore of the metal. It may be formed in the laboratory by heating together three parts of granulated lead and one part of

for more severe cases strong emetics, followed by active purgatives; and cataplasms applied to the stomach have been used with good results. For the purpose of calming the pains, incident upon the disease, chloroform and opium have been recommended.

In cases of poisoning by swallowing any preparation of lead; the patient should first be made to vomit by administering 10 to 15 grains of sulphate of zinc, or 20 to 30 grains of ipecacuanha, and by irritating the throat about the root of the tongue. This must be followed by a dose of the sulphate of soda, or sulphate of magnesia (Glauber salts or Epsom salts), which converting the soluble salt of lead into an insoluble sulphate, renders it inactive.

sulphur, or, as has already been remarked, by adding to a solution of one of the salts of lead a soluble sulphide, or treating it with a current of sulphuretted hydrogen.

It is quite fusible, but less so than metallic lead. It cannot, however, be kept in fusion a long time in earthen crucibles, since, like litharge, it destroys them, but a crucible of carbon will retain it.

It is much more volatile than lead, and its disposition to go off in vapour is much increased by passing over it a stream of gas.

Nitric acid attacks and changes galena to a sulphate, the other acids do not appear to affect it, except strong hydrochloric, which, when heated, converts it into a chloride.

Roasting in contact with a current of air transforms galena into a mixture of the *oxide* and the *sulphate* of lead, while fumes of sulphurous acid are given off.

When galena is fused with metallic iron, copper, antimony, or zinc, it is decomposed with the formation of metallic lead.

When iron is used in this connection the lead may be almost entirely separated from the sulphur, and, since the tendency of iron to alloy with lead is very slight, in a state of almost complete purity. *If the galena contain at the same time sulphide of silver, it will experience the same decomposition, and the lead and silver will be found in the form of an alloy, while the iron will be converted into the sulphide.* This reaction is frequently taken advantage of for obtaining rich lead upon a large scale. It forms the basis of the method employed on the Hartz, in various parts of central Germany, in Hungary, and in Sweden.

When a mixture of galena and the oxide of lead are fused together, there is a mutual decomposition; and if the proper proportions are employed, all the sulphur will go off as sulphurous acid gas, and only metallic lead will remain.

Thus, if 53·6 parts of galena (representing one atom) and 100 parts of the oxide of lead or litharge (representing two atoms) are, while in contact, brought to a white heat, the sulphur and oxygen combine, forming sulphurous acid, and 139·2 parts of pure lead are obtained.

If *galena*, in this experiment, predominate, a portion of the sulphur will be combined, and a *sub-sulphide of lead* will remain; if, on the contrary, the *oxide of lead* is in excess, *metallic lead* and *litharge* will be the result; but when a mixture of the two substances is only raised to a heat just sufficient to fuse them, a *grey oxysulphide* will be obtained.

Galena and the sulphate of lead decompose each other mutually when brought to a red heat. Thus, 79 parts of galena (representing one atom) and 100 parts of sulphate of lead (representing one atom) will give sulphurous acid gas, which goes off, and 127 parts of pure lead.

If *galena* and an *excess* of the *sulphate of lead* be fused together, the *oxide of lead* will be obtained instead of the metal.

The *sulphate* and the *sub-sulphide* also react on each other, producing, according to the proportions employed, *metallic lead* and the *oxide of that metal*. If, in any of these cases, *silver* is present, either as an *oxide* or a *sulphide*, and *metallic lead* is produced, the *silver* will be reduced, and will be found alloyed with the lead.

These reactions are of immense importance to the lead and silver smelter, since upon them are founded the larger number and most extensively used methods of obtaining lead and "rich lead" from the ores of the two metals.

SULPHATE OF LEAD.

The sulphate of lead as formed in the laboratory is a white powder, insoluble in water, always anhydrous, and represented by the formula PbO, SO_3 . In nature it is found crystallised in octohedrons. Sulphuric acid partially dissolves it, taking up, when very concentrated, $\frac{1}{6}$ of its weight. Hydrochloric acid dissolves it, setting free sulphurous acid.

This salt is one of the results when galena is roasted in a current of air. It is almost the only one of the sulphates which is not decomposed at a high temperature; when brought to a white heat in a porcelain tube, its decomposition is only partial, and may be attributed to the action of the silicic acid of the porcelain.

Its important action in reduction of the ores of lead in metallurgic processes has been spoken of above. It may itself be reduced to the oxide by fusing with metallic lead; one atom of the metal acting upon one atom of sulphate, producing two atoms of litharge, and disengaging sulphurous acid gas. The sulphate of lead is not very fusible itself; but when mixed with $\frac{1}{8}$ th of its weight of litharge, it forms a compound, which, at a white heat, is as liquid as water. When fused with $\cdot 736$ its weight of oxide of lead, it produces a white or slightly yellow mass, which is the subsulphate, $2\text{PbO} + \text{SO}_3$. The sulphate of lead is prepared on a large

scale, and is used in printing calicoes and in glass making.

CARBONATE OF LEAD.

The carbonate of lead (PbO, CO_2) is a white salt, which forms beautiful rhombic crystals in nature, but which is best known as a powder, or, mixed with oil, under the name of *white lead* or *ceruse*. It is insoluble in water. When heated in the air it loses its acid, and goes over into a species of *minium*, which possesses a lively colour, exceeding that of ordinary minium. The manufacture of carbonate of lead is carried on on a large scale, and by two processes which will be spoken of in a subsequent chapter. White lead forms the base of almost all species of painting in oil, and vast quantities of lead are yearly converted into it.

CHROMATE OF LEAD.

This is a beautiful yellow salt, insoluble in water, and with difficulty soluble in acids. It is formed by precipitating the chromate of potash with the nitrate or acetate of lead. Painters employ it considerably with oil, and calico-printers and confectioners use it as a colouring matter. The commercial article is frequently adulterated with a quantity of plaster of Paris, which appears to heighten its effect as a pigment.

The composition known as *Cologne yellow* consists of 15 parts of sulphate of lead, 60 parts of plaster of Paris, and 25 parts of the chromate of lead.

CHAPTER V.

THE ORES AND MINERALS CONTAINING SILVER AS AN ESSENTIAL
CONSTITUENT.

THE extremely high comparative value of silver makes it possible to treat metallurgically with profit compounds containing but a very small quantity of the metal. The average of the copper ores of Cornwall is between 6 and 7 per cent., the lead ores of Great Britain average about 71 per cent.; those about Clausthal in the Hartz, 59·9; and when the natural products from which these two metals are drawn yield in the latter case 25 to 35 per cent., and in the former 1 to 2 per cent., they are deemed extremely poor, and can only be worked with profit under peculiar circumstances. But the poorest ores of copper and lead hold a larger weight of valuable metal than what are considered very rich silver ores. The ores of Joachimsthal, which average among the highest in Europe, generally hold about 2 or 3, and seldom exceed 10, per cent. of silver. The average of the region about Clausthal is 0·098 per cent., and that of Andreasberg is 0·36 per cent. At Freiberg, though frequently very rich ores are obtained, the perfection of the system of smelting allows extremely poor minerals to be worked with profit. Thus where silver is the only valuable constituent present, and that to the amount of ·05 per cent. ($\frac{1}{2000}$), the ore is considered worth purchasing by the smelting department, and when lead to the amount of 35 per cent., or copper to the amount of 5 per cent., is present, the silver, if it reaches a ·01

per cent., is paid for. The average quantity of silver in Mexican ores is stated by Rivot to be about 0.25 per cent., and the rich ores of Zacatecas, which are sent to the establishments for amalgamation, do not reach 0.50 per cent.

These figures show that a mineral, of which $\frac{9999}{10000}$ of the mass of which consists of earths or the compounds of the baser metals, may, under certain circumstances, be considered *an ore of silver*. Hence the list of substances claiming a place under this head is very large.

The following pages contain a description of all the natural compounds of silver and lead, to which the attention of the metallurgist will be likely to be called, with their physical characteristics, and a notice of such chemical peculiarities as is necessary for rapid blow-pipe examination. The proportion of metal given is, as a rule, that which exists when the mineral is entirely pure.

A. *Silver Uncombined.*

Native Silver is usually found alloyed with a small quantity of copper, iron, gold, platinum, or antimony. Its lustre is metallic; colour and streak, silver white; hardness 2.5 to 3; specific gravity, 10.1 to 11.1. Ductile and malleable, usually in fine or coarse threads; arborescent or massive; crystallisation, monometric. Before the blowpipe (B. B.) it fuses rather easily upon charcoal to a button. It is soluble in nitric acid, and is readily deposited from its solution upon a plate of copper.

The filiform varieties are often composed of one or more series of octohedrons closely united and ranged in rows. This structure may be observed in many specimens from Norway and Mexico. In a few mines it is

almost the only ore of silver explored, as at Kongsberg in Norway, and in the Lake Superior copper districts. In the latter region it is found isolated in the masses of native copper without being chemically combined. The mines of Kongsberg have afforded magnificent specimens of this variety. One mass from that locality in the royal collection at Copenhagen weighs upwards of 5 cwt., and recently two blocks have been obtained weighing respectively 238 and 436 pounds. Much of the silver of Peru has been found in a native condition; a mass discovered at Huantaya weighed 800 pounds. But all these are surpassed by an immense mass discovered in Sonora, which, we are told by Wilson, weighed 2700 pounds, and was the subject of a suit brought by the King's Attorney, who sought to recover it on the plea that it was a curiosity, and belonged to the Crown.

B. Silver Combined with other Metals.

Bismuth Silver.—A compound containing a variable quantity of silver; analyses give from 15 to 60 per cent. Lustre metallic, colour white; texture, usually amorphous. B. B. readily fuses to a silver button, and covers the charcoal with the oxide of bismuth, and when lead is present, with the compounds of that metal. Occurs in Chili, Baden, and Thuringia, and was at one time worked as an ore of silver.

Amalgam (AgH_2) with 34·8 per cent. of silver, or (AgH_3) with 26·25 per cent. of silver and 75·75 per cent. of mercury. Colour and streak, silver white; hardness, 3 to 3·5; specific gravity, 10·5 to 14; brittle; gives a grating sound when cut with a knife, crystallises

monometric. B. B. the mercury evaporates, and silver is left; dissolves in nitric acid. When rubbed on copper imparts a fine silvery lustre. Occurs in various parts of Germany, in France, Spain, and Chili.

Antimonial Silver (AgS_3). — Silver 77 per cent.; lustre, metallic; colour and streak, white, opaque; fracture, uneven; hardness, 3·5 to 4; specific gravity, 9·4 to 9·8; crystallisation, trimetric. B. B. fuses easily to a grey brittle bead, giving off antimonial fumes, and at last a malleable silver bead is obtained. Dissolves in nitric acid, leaving a white powder behind. Occurs in small quantities among the ores of silver at Andreasberg in the Hartz, also in Dauphiné, and near Coquimbo, South America.

C. *Silver in Combination with Tellurium.*

Telluric Silver (AgTe).—Silver 62·8 per cent.; lustre, metallic; colour, lead or steel grey; hardness, 2 to 3·5; specific gravity, 8·3 to 8·9, slightly malleable. B. B. on charcoal gives fumes at a high heat, and leaves a somewhat brittle bead of silver. With soda reduces to pure silver. Occurs in Siberia in a talcose rock with pyrites and blende. Specimens have been obtained a cubic foot in size.

D. *Silver in Combination with Selenium.*

Selenide of Silver (AgSe).—Silver, 73·2 per cent.; lustre, metallic, splendid; colour and streak, iron black; hardness, 2·5; specific gravity, 8; crystallises in cubes; cleavage, cubic and perfect. Fused in a glass tube, gives a slight red sublimate. B. B. with soda or borax

yields a silver globule. Occurs at Tilkerode, in the Hartz.

Eucairite ($\text{Cu}_2\text{Se} + \text{Ag Se.}$) — Silver 43.1 per cent.; lustre, metallic; colour, between silver white and lead grey; streak, shining, so soft that it may easily be cut with a knife. Occurs massive or in films. B. B. gives off copiously fumes of selenium, and on charcoal fuses easily to a grey metallic globule; with borax gives a copper reaction. This mineral is found in calcareous spar at Skrikerum copper mine in Sweden.

E. Silver in Combination with Sulphur and the Sulphides.

These compounds are found widely disseminated in nature associated with native silver, blende, sulphide of antimony, or the ores of cobalt and nickel. In Mexico they are quite abundant, and constitute the black ores or *negros* of the miner, which should be submitted to a preliminary roasting before being given to the amalgamation. They usually contain a small quantity of gold, and this metal may be expected in larger proportions whenever pyrites is present, either intact or altered by the atmosphere.

In general these ores cannot be concentrated by washing without losing much silver, and particularly is this the case when much antimony or arsenic is present as a mineraliser. The portions richest in silver are then extremely brittle, and they break beneath the stamps, or between the rollers, to such minute particles that the water carries a large quantity away in suspension. The most economical means of obtaining a rich material for the furnace is by sorting by hand. Galena,

which is one of the most important minerals from which silver is extracted, will be found fully described in the following chapter.

Silver Glance (AgS), silver 87.1 per cent.; lustre, metallic; streak and colour, blackish lead grey; fracture, uneven; occurs reticulated, arborescent, filiform, and amorphous; crystallisation in the monometric system. B. B. Intumescs, and on charcoal soon affords a globule of pure silver. Soluble in nitric acid with the deposition of sulphur. It is so fusible that it readily yields to the flame of an ordinary candle. This is one of the most important of the natural compounds of silver. It is a frequent ore in the mines of the Hartz, Saxony, Bohemia, Mexico, and is also found in Cornwall, and in the United States.

Stephanite ($6\text{AgS} + \text{SbS}_3$), with 71 per cent. of silver; lustre, metallic; colour and streak, iron black; fracture, uneven, sectile; hardness, 2 to 2.5; specific gravity, 6.27. Massive, compact and disseminated, crystallises in the trimetric system. Decrepitates when heated; fuses in a closed glass tube, and gives a slight sublimate of sulphide of antimony. B. B. forms a dark-coloured metallic globule, which may be further reduced by the addition of soda. This important ore of silver is obtained from the mines of Saxony, Bohemia, and Hungary, and is probably the principal form in which silver occurs in the new mines of Washoe in Sonora. It is also found in the Hartz, at Zacatecas, and in Peru.

Polybasite.—This is a mineral containing 75.2 per cent. of silver in combination with copper, antimony, arsenic, and sulphur. Lustre, metallic; colour and streak, iron black, by transmitted light it sometimes appears red. Crystallises in the hexagonal system, and

possesses an imperfect basic cleavage. Occurs also massive and disseminated. B. B. decrepitates somewhat, fuses easily, on charcoal gives a coating of the oxide of antimony and the reaction of copper. It is found in the mines of Freiberg, Hungary, and Cornwall.

Dark red Silver Ore, or *Ruby Silver* ($3\text{AgS} + \text{SbS}_3$), with 59 per cent. of silver; lustre, metallic adamantine; colour, black, sometimes approaching cochineal-red; streak, cochineal-red, translucent to opaque. Crystallises in the rhombohedral system, and also occurs massive, with a granular structure. B. B. fuses, and gives off fumes of antimony, and ultimately on charcoal a globule of silver. Dissolves in heated nitric acid, leaving a residue of silver and oxide of antimony. Occurs with calcareous spar and native arsenic at St. Andreasberg on the Hartz, also in Cornwall, Saxony, Hungary, and Spain.

Xanthocone, a compound of 64 per cent. of silver, with sulphur and arsenic; colour, dull red, or clove-brown; crystals, orange-yellow on the edges by transmitted light; streak, yellow; hardness, 2; specific gravity, 5 to 5.2; usually occurs in reniform masses, with an interior coating of minute crystals. Is found near Freiberg in Saxony.

Light red Silver Ore ($3\text{AgS} + \text{AsS}_3$), lustre, adamantine; colour and streak, cochineal-red, subtranslucent; fracture, conchoidal or uneven; specific gravity, 5.42; hardness, 2.25; crystallisation, rhombohedral. B. B. on coal gives at first vapours of arsenic, and then sulphurous fumes, and produces a globule which, when treated with soda, gives pure silver. It is found in Saxony and in Bohemia, also at Guadalcanal in Spain.

Sulphide of Silver and Copper ($\text{Cu}_2\text{S} + \text{AgS}$), with

53·1 per cent. of silver; colour, dark steel-grey, metallic; streak, shining; fracture, subconchoidal; hardness, 2·3 to 3; specific gravity, 6·2. Crystallises in the trimetric system. B. B. fuses easily to a grey metallic globule, and with fluxes gives the red copper bead. Dissolves in nitric acid, affording a blue solution. It occurs in Siberia, Silesia, in Chili, and in the Heintzelman mine in Arizona.

Mairgyrite ($\text{AgS} + \text{SbS}_3$), with 35·9 per cent. of silver; lustre, submetallic, adamantine; colour, iron-black; streak, dark cherry-red, opaque, except in thin splinters, which by transmitted light are deep blood-red; fracture, subconchoidal, very sectile; crystallisation, monoclinic. In an open tube fuses easily, and gives a sublimate of the oxide of antimony, and at the same time develops sulphurous acid. B. B. reduces to a globule of silver. Occurs near Freiberg in Saxony.

Sternbergite; a compound of nearly equal parts of silver, sulphur, and iron; lustre, metallic; colour, pinchbeck-brown; streak, black; hardness, 1 to 1·5; specific gravity, 4·21; thin lamina, flexible; crystallises trimetric, cleavage perfect. Occurs usually in implanted crystals. B. B. on charcoal burns with a blue flame and melts to globule, which is generally hollow, and attracts the magnet. With borax, a globule of silver may be obtained. Is found at Joachimsthal in Bohemia, and in Saxony.

Freislebenite, a compound of sulphur, antimony, lead, and silver, containing of the latter about 22 per cent.; colour and streak, light steel grey, inclined to silver white, yields easily to the knife, brittle; lustre, metallic; hardness, 2·25; specific gravity, 6 to 6·4. B. B. on charcoal emits copious white vapours and a slight sulphurous

odour, and deposits a coating of the oxides of antimony and lead around the assay. Occurs near Freiberg in Saxony, and in Transylvania.

Grey Copper, a compound of silver, copper, iron, zinc, antimony, and sulphur in which the quantity of silver varies largely; a specimen from Freiberg gave 31 per cent., sometimes this metal is almost entirely wanting. Colour, between steel-grey and iron-black; streak, sometimes inclined to brown, but generally the same as the colour; texture, closely granular and compact; lustre, metallic; hardness, 3 to 4·5; specific gravity, 4·5 to 5·1. Heated in a closed glass tube, melts sometimes with decrepitation, and gives, with a very strong heat, a dark red sublimate of the sulphide of antimony. When the ore contains quicksilver, as is sometimes the case, the sulphide of that metal is sublimed at a low red heat, and collects on the glass in the form of a dark ring. B. B. on charcoal melts easily to a bead, gives off much vapour, and covers the coal with the white oxide of antimony. The silver that may be present is sought by melting the roasted ore with lead and borax glass, and cupelling. The mines of St. Austel in Cornwall, of Cabarras Co. North Carolina, of Clausthal in the Hartz, of Freiberg, and Transylvania afford this ore.

*F. Silver in combination with Chlorine, Bromine,
and Iodine.*

This class of ores, though at one time considered rare, has been found to constitute a valuable portion of many veins. They are generally found disseminated in a different part of the deposit from that in which the sulphides are found, and associated with clay,

quartz, calc spar, and baryta. At Huelgoet in Brittany, they constitute the ore known as *terres rouges*, which, with an average of $\frac{1}{20}$ th of 1 per cent. of silver, are subjected to amalgamation. In Spain the chloride appears to have existed in considerable quantities at the mines of Guadalcanal. In Chili, Peru, and Mexico large quantities of this class of ores are worked. The veins in which they are found usually contain sulphides, arsenides, and compounds of antimony in their lower portions. The chloride, iodide, and bromide, and native silver compose a very valuable part of the ores known as *Colorados* in South America and Mexico, and which are treated *directly* by the process of amalgamation in heaps.

Chloride of Silver (AgCl), with 75·3 per cent. of silver; lustre, resinous, passing into adamantine; colour, pearl-grey, greenish, rarely bluish, brown on exposure; streak, shining, translucent; fracture, somewhat conchoidal, sectile; crystallisation, monometric, but usually massive, and looking like wax; hardness, 1 to 1·5; specific gravity, 5·4 to 5·5. Fuses in the flame of a candle, with the emission of acrid fumes. B. B. on charcoal easily reduced to a silver globule. If rubbed with a plate of moistened iron, the iron becomes covered with a thin film of metallic silver; not soluble in nitric acid or water. The most important localities of this ore are in Chili, Peru and Mexico. It has also been found in the mines of Norway, Saxony, Siberia, the Hartz, and Cornwall.

Iodide of Silver (AgI), with 46 per cent. of silver; lustre, resinous to adamantine; colour, citron to sulphur yellow; streak, yellow; translucent, plates flexible; crystallisation hexagonal, also occurs with a lamellar

structure; specific gravity, 5·5. B.B. on charcoal fuses immediately, producing a vapour which tinges the flame a fine violet colour, reduces to a globule of silver. This ore occurs in various parts of the New World. At Abarradon in Zacatecas it is found in thin veins in steatite.

Bromide of Silver (AgBr), with 57·7 per cent. of silver; lustre, splendid; colour, when pure, bright yellow, often grass or olive-green externally; hardness, 1 to 2; specific gravity, 5·8 to 6; crystallises in cubo-octohedrons. B.B. fuses easily, imperfectly dissolved by acids but soluble in heated concentrated ammonia. Occurs at Huelgoet in Brittany, and in the district of Plateros, Mexico, near Zacatecas, where it is so abundant that the ores have received the name *plata verde*, from the colour it causes them to assume. It is also found in Chili.

ORES CONTAINING SILVER IN A VARIABLE PROPORTION, AND NOT AS AN ESSENTIAL CONSTITUENT.

A number of the natural compounds of other metals often hold silver in a greater or less proportion, and in such cases it is made either partly or wholly the object of the metallurgic operations to which these ores are subjected. Among these may be mentioned the following:—

Zinc Blende, with as much as 0·88 per cent. of silver.

Iron Pyrites sometimes contain ·15 per cent.

Native Arsenic.—In Saxony this mineral has been found with ·047 silver, and in the Hartz, at St. Andreasberg, it contains ·5 per cent. of silver, and the remainder in the furnaces after the treatment for

arsenious acid, is profitably worked for the precious metal.

Misspickel sometimes contains .038 per cent. of silver, and the compounds of sulphur and antimony, and arsenic, with nickel and cobalt, often contain some silver, when ores of that metal occur in the same vein.

CHAPTER VI.

THE ORES AND MINERALS CONTAINING LEAD AS AN ESSENTIAL CONSTITUENT.

THE natural compounds of lead which occur in such abundance and purity as to be of much importance to the smelter, are exceedingly limited in number. Almost all the lead of commerce is obtained from the following five minerals: galena, the carbonate, the sulphate, the phosphate, the arseniate; and the first-mentioned of these furnishes far more metal than all the others combined.

The metallurgist, however, finds, more or less abundantly, among his ores, lead-bearing minerals, the nature of which it is always interesting, and often quite useful, for him to understand. The subjoined list includes all that he will be likely to meet with, and at the same time gives the physical and chemical characteristics by which they may be distinguished.

A. *Lead Uncombined.*

Native Lead.—This rare substance is found in thin plates and small globules. Its characteristics are very

similar to those of ordinary commercial lead. It has been shown by analysis to be extremely pure. Hardness, 1·5; lustre, metallic; colour, lead-grey; crystallisation, monometric. B. B. fuses easily, covering the charcoal with a yellow oxide. It has been found with galena at Kerry, in Ireland, at Alston Moor, and in lava in Madeira.

B. Lead combined with Tellurium.

Telluride of Lead (PbTe), with 61·7 per cent. of lead; lustre, metallic; colour, tin white; occurs usually massive, and rarely in cubes; cleavage, cubic. B. B. volatilises in the reducing flame, and colours the flame blue. It usually contains a little silver, which remains upon the coal. Soluble in nitric acid. This species is found at Savodinsky, in the Altai, with telluric silver.

C. Lead in combination with Selenium.

Selenide of Lead, with 72·4 per cent. of lead; lustre, metallic; colour, lead-grey, somewhat bluish; streak, darker, opaque; fracture, granular and shining, rather sectile. Occurs in fine granular masses, crystallises in the monometric system; cleavage, cubic; hardness, 2·5 to 3. B. B. Heated on charcoal, gives off the odour of horse-radish, and forms a coating of the oxide of lead. This is a rare species, found in several mines in the Hartz, and at Freiberg, in Saxony. The compound of lead and selenium has occasionally an admixture of cobalt, copper, or quicksilver, which among some mineralogists have received special names, and are known as distinct species.

D. Lead in combination with Sulphur.

Galena, Sulphide of Lead (PbS), contains, when perfectly pure, 86·6 per cent. of lead, and 13·4 per cent. of sulphur. Lustre, metallic; colour and streak, pure lead grey. Crystallises in cubes, and in the various modifications of the monometric system. Cleavage, cubic and perfect; texture, coarsely or finely granular, sometimes impalpable, and occasionally fibrous. Hardness, 2·5 to 2·75; specific gravity, 7·25 to 7·7. Decrepitates when heated, and gives in the open tube sulphurous acid and a sublimate of sulphur and sulphate of lead. B. B. on charcoal fuses, gives off sulphurous fumes, and produces a globule of lead, which, if cupelled, will usually afford a minute quantity of silver. In hot hydrochloric acid it dissolves slowly, and upon cooling, chloride of lead crystallises out. Galena is the most important ore of lead, and at the same time one of the most important sources of silver. The latter metal is present in the condition of a sulphide, and recent experiments lead to the conclusion that no galena is entirely free from it, though in some cases it exists in extremely small quantities. It is not determined whether the sulphide of silver exists mechanically mixed or chemically combined with the sulphide of lead. There is a general belief among miners that the fine-grained varieties of this ore are rich, and the coarse-grained varieties poor in silver, but although this law may apply to the minerals of a particular locality, it is so often contradicted that it cannot be considered as general. Galena is found in nearly every country of the globe, and in nearly all the geological formations. In Cornwall it is found in veins in the killas, and the

rich deposits of Cumberland, Derbyshire, and the northern districts of England, are in the mountain limestone. At Freiberg, in Saxony, it occupies veins in gneiss; at Sala, in Sweden, it occurs in granular limestone. In Cardiganshire and Montgomeryshire it is found in strata of the Lower Silurian age, and the chief deposits in the United States have been discovered in rocks belonging to the same geological epoch. Galena occurs sometimes quite free from veinstone, and sometimes largely mixed with various metallic sulphides or earthy minerals. In English mines it is usually associated with calcareous spar, pearl spar, fluor spar, heavy spar, wetherite, calamine, and blende. In the deposits of the Mississippi valley it is associated with carbonate and sulphate of lime, blende, calamine, pyrites, and often an ore of copper and cobalt. In the Hartz, with calcareous spar, quartz, heavy spar, and spathic iron. The pyrites which accompanies galena is often auriferous; it appears to contain the gold in a native state. Quartz is sometimes intimately mixed with galena, and even the most careful washing cannot entirely separate them. In such a case, the treatment for lead will be essentially modified, since where much quartz is present, the use of the reverberatory furnace must give place to that of the cupola. Fluor spar and calc spar are generally not mixed in minute particles with the ore, and hence they may be separated almost completely by hand sorting. A small quantity of lime will not act deleteriously in the operations in the reverberatory furnace. The sulphate of baryta, on account of its very high specific gravity, is extremely difficult to separate from galena by the usual processes of washing. The feldspathic and argiliferous minerals that some-

times accompany this ore of lead, occasion nearly the same difficulties as quartz, and where they cannot be well separated by washing or sorting, the cupola furnace should be employed in their treatment.

The sulphide of iron is often so intimately mixed with galena, that it is impossible to treat it by the reverberatory furnace. The ores of Rammelsburg, in the Hartz, may be mentioned as belonging to this class. The sulphide of antimony, where it occurs in a finely-divided state with galena, cannot be separated by dressing. It interferes with the treatment by *double decomposition*, and produces an impure lead. When the sulphide of lead is mingled with copper pyrites, the lead produced is always cupreous, and in the subsequent cupellation the copper is oxidised with the lead, and an impure and less valuable litharge is produced. The carbonate of iron, which is frequently found in connection with galena, is not a mineral to be feared by the furnace-man, since it usually occurs in such large pieces, that it may be readily sorted out by the hand; and in the reverberatory furnace, a small quantity is not injurious, while it is frequently added as a flux in smelting in the cupola furnace.

The amount of lead contained in the sulphurous ores worked at various furnaces, is exceedingly variable. Where lead is the only valuable metal present, it is necessary that it contain a comparatively large percentage to repay the cost of treatment. At Freiberg, as has already been mentioned, ores containing less than 35 per cent. of lead, and no other valuable constituent, are not bought. If, however, 5 per cent. of copper, or $\frac{1}{20}$ th per cent. of silver, is present, as soon as the lead exceeds 15 per cent. it is paid for. At

Rammelsberg much ore is smelted with less than 10 per cent. of lead, but, besides that metal, silver, gold, copper, zinc, sulphur, and several other products, are obtained from the same mass. The average of the galena brought to the furnaces at Bleiberg, in Carinthia, is between 65 and 72 per cent. The furnaces of Flintshire employ an English ore giving by assay between 70 and 78 per cent. of lead.

The silver contained in galena seldom exceeds 1 per cent.

Geocronite ($5 \text{ PbS} + \text{SbS}_3$) with 66.8 per cent. of lead; colour and streak, light lead grey; fracture, uneven; crystallises trimetric, but usually occurs massive. Also granular or earthy; hardness, 2 to 3; specific gravity, 6.4 to 6.6. B. B. fuses readily, gives off fumes of antimony and sulphur, and coats the charcoal upon which it is fused yellow. Occurs in the silver mines of Sala, in Sweden, in Tuscany, and at Kilbricken, Clare county, Ireland.

Boulangerite ($3 \text{ PbS} + \text{SbS}_3$) with 58.0 per cent. of lead. Occurs in plumose specimens, exhibiting in the fracture a crystalline structure, generally massive, also granular and compact. Hardness, 2.5 to 3; specific gravity, 5.75 to 6.0. B. B. fuses readily, with exhalations of sulphurous acid and fumes of oxide of antimony. On charcoal a yellow coating indicates the presence of lead. This species is found in some abundance at Molières, Department of Gard, in France, also in Lapland and Tuscany.

Jamesonite ($3 \text{ PbS} + 2 \text{ PbS}_3$) with 43.6 per cent. of lead. Cleavage, highly perfect; crystallises in trimetric prisms, occurs also massive and columnar, particles delicate; lustre, metallic; colour and streak, steel grey. B. B. on charcoal decrepitates, fuses readily, and

almost wholly passes off in fumes. Occurs principally in Cornwall, associated with quartz and minute crystals of Bournonite.

Bournonite ($[3\text{Cu}_2\text{S} + \text{SbS}_3] + 2[3\text{PbS} + \text{SbS}_3]$) with 41.8 per cent. of lead; lustre, metallic; colour and streak, steel grey, sometimes inclined to lead grey or iron black; fracture, conchoidal or uneven; crystallisation, trimetric; hardness, 2.5 to 3; specific gravity, 5.7 to 5.9. B. B. decrepitates, fuses easily, and gives off sulphur and antimony fumes. In a strong heat the charcoal is covered with oxide of lead, dissolves readily in nitric acid, forming a blue solution. First found at Endellion, near Redruth, in Cornwall. Occurs also at Beeralston, in Devonshire, in the Hartz, and near Freiberg, in Saxony.

E. *Lead in combination with Chlorine.*

Chloride of Lead (PbCl_2), with 74.5 per cent. of lead. A soft white adamantine substance, crystallising in trimetric prisms. Observed in the crater of Vesuvius after the eruption of 1822.

Mendipite ($\text{PbCl}_2 + 2\text{PbO}$); lustre, pearly, and somewhat adamantine on the cleavage faces; crystallisation, trimetric; cleavage, highly perfect; hardness, 2.5; specific gravity, 7; colour, white, with a tinge of yellow, blue, or white; streak, white. B. B. decrepitates slightly, and readily fuses. On charcoal lead may be obtained. When treated with salt of phosphorus and the protoxide of copper, the flame assumes an intensely blue colour. This rare mineral occurs at Mendip Hills, in Somersetshire, and in Silesia and Westphalia.

F. Lead in combination with Oxygen.

Lead Ochre (PbO), with 92·83 per cent. of lead. A massive, dull, yellow mineral, with occasionally a scaly structure. It is said to be ejected from the volcanoes of Popocatepetl, in Mexico, and it is found in many places in the provinces of Chihuahua and Cohahuila. It also occurs at Hustin's Mines, in Wythe County, Virginia.

Minium (Pb_3O_4), with 90·66 of lead. A red powdery mineral, from Anglesey, and Grassington Moor, and Wierdale, in Yorkshire.

G. The Oxide of Lead in combination with Acids.

Sulphate of Lead (PbO,SO_3), with 73·6 per cent. of the oxide of lead. Colour, white, greyish, greenish, and sometimes bluish; lustre, adamantine; streak, uncoloured; fracture, conchoidal, transparent, to opaque; hardness, 2·7 to 3; specific gravity, 6·259 to 6·298; crystallisation, trimetric. Decrepitates in the flame of a candle, and frequently becomes slightly reddish. B. B. melts to a bead, which cools milk white, and in the inner flame affords metallic lead by the addition of soda. This mineral results in many instances from the decomposition of the sulphide of lead, and occupies the upper portions of veins. In some cases it appears to be accompanied with more silver than the galena in other parts of the deposit. Lead Hills and Wanlockhead afford large and beautiful crystals of this species. It is also found in Cornwall, Derbyshire, and in various parts of Germany, France, and America.

Linarite ($\text{PbO},\text{SO}_3 + \text{CuO},\text{HO}$) with 75·7 per cent. of

sulphate of lead, is an azure blue, adamantine mineral, which has been found at Linares, in Spain, at Rough-ton Gill, in Cumberland, and at Lead Hills. Its crystallisation is monoclinic; cleavage, perfect; streak, pale blue, and fracture conchoidal.

Caledonite, a cupreous sulphato-carbonate of lead, crystallising in trimetric prisms; colour, deep verdigris, or bluish green; hardness, 2·5; streak, greenish white. From Lead Hills, in Scotland, Linares, in Spain, and Missouri.

Lanarkite, a sulphato-carbonate of lead, from Lead Hills. Its colour is greenish white, pale yellow, or grey, transparent; streak, white, and it crystallises in the monoclinic system.

Leadhillite ($\text{PbO}, \text{SO}_3 + 2\text{PbO}, \text{CO}_2$), with 27·44 per cent. of sulphate, and 72·56 per cent. of carbonate of lead. A white, yellow, or greenish mineral, sometimes transparent, with specific gravity 6·2 to 6·5; hardness, 2·5, and crystallising in the trimetric system. Occurs principally at Lead Hills, but has been found in the United States, and on the Island of Serpho, in the Grecian Archipelago.

Phosphate of Lead ($\text{PbCl} + 3 [3\text{PbO} + \text{PO}_5]$) with from 69 to 76 per cent. of lead. The colour of this ore varies largely—green, yellow, and brown are its most frequent shades; streak, white or yellowish. Occurs crystallised in hexagonal prisms, and also fibrous and granular. Its hardness is 3·5 to 4, and specific gravity, 6·58 to 7. B. B. fuses easily, and colours the outer flame bluish green. When the globule thus formed cools, it assumes a polyhedral form. Dissolves readily in nitric acid. This mineral occurs in the upper parts of veins, where the galena has been decomposed by

atmospheric agency. The fact that it is found in deposits which in their original condition do not contain phosphates, has led to several hypotheses to account for its formation. It is probable that it results from the action of surface water charged with carbonic acid and phosphate of lime, upon the carbonate of lead. Fine specimens of this mineral come from Lead Hills and Wanlockhead, from Cornwall and Wicklow, from Phoenixville, Chester county, and it accompanies other lead ores in a large number of mines.

Arsenate of Lead ($\text{PbCl} + 3 [3\text{PbO} + \text{ASO}_5]$), a pale yellow, or brown mineral, that sometimes, from the presence of the chromate of lead, becomes orange yellow; streak, white; hardness, 3·5; specific gravity, 7·19 to 7·25; crystallisation similar to that of the preceding species, which it also resembles in occurring near the outcrop of veins. B. B. fuses to a brownish yellow mass, and on charcoal reduces to a globule of lead, giving off at the same time copious fumes of arsenic. This mineral is found at Wheal Unity, near Redruth, and at several other Cornish mines; also at Beeralston, in Devonshire, and Caldbeckfell, in Cumberland.

Carbonate of Lead (PbO, SO_3), with 68·3 per cent. of lead. A transparent or translucent mineral, with a white or greyish colour, that is sometimes tinged blue by the salts of copper; crystallises in the trimetric system, but occurs also granular and massive; lustre, adamantine, inclining to vitreous; streak, uncoloured; hardness, 3 to 3·5, and specific gravity, 6·46 to 6·48. B. B. decrepitates, becomes yellow, then red, and finally, with care, on charcoal, a globule of lead may be obtained. Dissolves in nitric acid with effervescence, and is also soluble in a solution of potash. This is the most abundant

of the oxidised ores of lead. It is raised in considerable quantities in several localities, as at Deepelinnen, near Aix-la-Chapelle, and in the neighbourhood of Santander, in Spain. This ore is often liable to be overlooked by the miner, or thrown aside as useless, its exterior resemblance to carbonate of lime, or earthy calamine, rendering such deception very easy. The above chemical tests, however, will at once determine its value. In general the carbonate of lead is not rich in silver; but where it results from the decomposition of argentiferous galena, it usually contains more silver than the original ore. In England fine specimens occur in Cornwall, at St. Minver's, and also at Lead Hills, Anglesey, and in Ireland at Seven-Churches, in Wicklow.

Chromate of Lead (PbO, CrO_3), with 68.7 per cent. of the oxide of lead. A beautiful, bright orange red mineral, with adamantine lustre, and orange yellow streak, translucent and sectile; hardness, 2.5 to 3; specific gravity 5.9 to 6.1, and crystallisation monoclinic. B. B. blackens and decrepitates if quickly heated, but may be fused to a shining glass, containing globules of lead. Dissolves with effervescence in nitric acid, producing a yellow solution. With soda yields readily metallic lead. Occurs in the Ural, in Hungary, and in Brazil.

The *chromate of lead and copper* is a rare species, with an adamantine lustre, and dark green or brown colour.

Molybdate of Lead (PbO, MO_5), containing 61.5 per cent. of the oxide of lead. Lustre, resinous and adamantine; colour, wax yellow, sometimes greyish and brownish; streak, white, and fracture sub-conchoidal; hardness, 2.75; specific gravity, 6.3 to 6.9; crys-

tallises in the dimetric system. B. B. decrepitates briskly, and becomes darker. With borax in the exterior flame it fuses readily to a slightly coloured glass. In the interior flame the glass is transparent, but on cooling it becomes all at once dark and opaque. This species occurs in limestone, with other lead ores, at Swarzenbach, Bleiberg and Windisch Kappel, in Carinthia; also in beautiful crystals at Phoenixville, in Chester county, Pennsylvania.

CHAPTER VII.

THE ASSAYING OF SILVER ORES AND OTHER ARGENTIFEROUS COMPOUNDS.

THE art of estimating the proportion of silver existing in a given sample of ore or manufactured product, has received, for so many generations, the attention of chemists and metallurgists, that an entire volume, such as compose this series, would not serve to describe all the methods that have been proposed, or even all that have been used, with more or less success. Until within comparatively few years fire was the exclusive medium employed for the purpose of refining the metal and bringing it to a condition in which it could be weighed and estimated. But two distinct methods are now in use, both of which play an important part among assayers.

- I. The estimation of silver by the "Dry way."
- II. The estimation of silver by the "Wet way."

THE ESTIMATION OF SILVER BY THE "DRY WAY."

The various processes in use for determining silver in this manner have in view the single object of producing

the metal in a pure condition, so that its amount may be readily found by weighing or measuring, and thus the quantity or per centage of metal in the original sample is at once known.

The processes, however, vary somewhat with the richness of the ore or product, the nature of the impurities present, and the quantity of the ore assayed. They may be conveniently studied under the following divisions:—

- 1st. *The assaying of ores and furnace products excepting alloys.*
- 2d. *The assaying of the alloys of silver.*
- 3d. *The assay with the blowpipe.*

I.—THE ASSAYING OF ORES AND FURNACE PRODUCTS EXCEPTING ALLOYS.

As in the metallurgic methods most generally in use for the working of silver ores on a large scale, the first object of the assayer, after a proper sample has been furnished him, is to collect, by fusion, all the silver it contains, in a mass of lead bearing a proper proportion to the weight of silver present, then to turn all the lead into an oxide, and thus obtain the two substances in a separate condition.

The work thus divides itself into two periods:—

Firstly—The ore or product is fused with an addition of lead (if enough of that substance is not already present), and with other fluxes; all foreign materials, if possible, are turned into a slag or volatilised, and the unadulterated alloy of lead and silver obtained.

Secondly—The period of *cupelling*, in which the argentiferous lead is brought upon a porous and refractory cupel or shallow crucible, fused and exposed to

a current of heated air. The lead is thus converted into litharge, which melting, is absorbed by the porous cupel, while the silver, on account of its less active attraction for oxygen, remains behind as a bright globe, which may be weighed, and from this weight the per centage of silver in the sample readily calculated.

FUSION FOR OBTAINING RICH LEAD IN THE DETERMINATION OF SILVER.

The proceeding here must be varied with the richness of the ore and the nature of the substances with which it is mixed. The sample, which has been selected with the utmost care, that a good average specimen of the whole heap or parcel may be obtained, is dried at a temperature of about 212° , that all the moisture may be driven off, and after weighing may generally at once be fused, without being subjected, as is the case with many other ores, to a preliminary roasting.

Before going further, it will be necessary to examine the nature and function of the fluxes used in this process.

1. *Test Lead*.—This should be of the purest quality that the market affords, and especial care must be taken to secure it as free as possible from silver. It is often difficult to obtain a suitable lead, since nearly all of that article in commerce contains a trace of the precious metal. The quantity present should always be determined by previous experiment, in order that the weight of silver added in the lead during the course of the assay may be subtracted from the weight of the final grain.

The assayer has always a store of this lead in his

laboratory, where it is kept in a finely divided granular form, and instead of weighing the amount necessary for each experiment, he may measure it with a spoon holding with approximate accuracy a quantity of a known weight.

The nature of the ore under treatment, as, for instance, *the proportion of lead already present*, the *amount of silver contained in the specimen*, and the *nature of the impurities to be slagged off*, all must be considered in making the addition of lead to the assay. If the only metalliferous substance mixed with the silver be a compound of lead, it may be unnecessary to make any addition; if much zinc or iron are present, the quantity of lead should be raised, and if copper, tin, cobalt, or nickel are largely among the impurities, even as much as twenty times the weight of the ore may be required. In common cases, however, from 8 to 12 times the weight of the ore will be found sufficient.

2. *Litharge*, or oxide of lead, is often used as a flux, and the same precautions should be exercised for securing a pure article as are necessary in the selection of test lead.

3. *Borax*.—This substance is added when the ore is of a basic nature to form a slag and produce a more fusible compound. An addition of too much is a disadvantage, since it covers the fused metals with a coating that excludes the air, and thus prevents the formation of the oxide of lead, that is essential for a proper reduction of the sulphides which may be present. The quantity of borax should be greater for the ores containing iron, lime, and baryta, and less for such as have an abundance of quartz or alumina. The amount added may vary from 0 to 50 per cent.

4. *Glass*, or *quartz*, is sometimes added to very basic ores, chiefly, however, with the view of preventing the crucible from being destroyed too rapidly.

5. *Charcoal*, in the form of a fine powder, is of use in some cases.

6. *Iron*, in the condition of small nails or bits of wire, is added occasionally with litharge. It forms by oxidising a fluid slag, and also assists in the decomposition of the arsenides, antimonides, and sulphides.

7. *Carbonate of Potash* and *Carbonate of Soda* are also occasionally in use, and *Saltpetre* has been employed as a flux where a strong oxidising agent is required.

Manipulation in the fusion for rich lead.

The system of preparing the alloy of lead and silver above spoken of, which is sanctioned by very general use, is that of *scorification* or *slagging*. It is applicable to all argentiferous products, is the most accurate of the methods by the dry way, and is consequently here particularly described.

The assayer should first determine, by a careful washing, or by a few qualitative blowpipe experiments, the approximate nature of the ore or product that he has submitted to him; this will be necessary in order to give him the needful data to regulate his subsequent course. For many ores simply the appearance of the powder is sufficient to enable the experienced assayer to go forward without further investigation.

The fusing cup or crucible used is best formed as in the accompanying cut. It should be $1\frac{1}{8}$ " high, and $2\frac{1}{2}$ " in greatest diameter, and formed of refractory fire-

clay. The proper quantity of ore and lead are placed in this cup, half the lead being put in the bottom, the ore placed upon this layer, and the remaining half brought on above. The size of the sample taken varies with the amount of silver it contains, and the accuracy with which it is deemed necessary to make the assay. From 50 to 400 grains are weighed out, as the circumstances may be; but when a large quantity is used, the above-described cups will be found too small.

When the ore is a nearly pure argentiferous galena, it is the practice in the Saxon works to add six times its weight of lead. Zinciferous ores should receive from 10 to 16 times, and cupreous ores 10 to 20 times the weight of the mineral taken, or so much that there may be 16 to 17 times as much lead as copper present. Upon the top of the lead last added 10 to 30 per cent. of borax is strewn, and the assay is now ready for the fire.

The "muffle furnace" is the form best adapted for carrying out the slagging and cupellation of lead; that figured at page 74 of the "Rudimentary Treatise on the Metallurgy of Copper" has been found to possess many advantages. It can be heated with stone coal, and the muffle in which the cups are placed is large enough to hold about thirty assays at once. This is found the most economical form at Freiberg, where a vast number of assays are made.

The cups containing their charges of ores and fluxes are placed in the furnace, arranged in such a manner that each assay may be known as corresponding to the record belonging to it in the assayer's note-book, the

muffle closed, and a strong fire is given to bring the charge to a fluid condition.

In ten to fifteen minutes the assays have melted, and now the muffle is opened and a stream of air allowed to enter. The lead is oxidised, and dissolves in this condition the oxides of the other easily oxidisable metals. When there is not enough borax present, the attendant observes an infusible skin swimming upon the surface, and he at once adds 10 to 15 per cent. of the flux to dissolve these impurities, which generally consist of various earths.

In ten or fifteen minutes the coating of fluid oxide of lead has extended over the whole, or nearly the whole surface of the metallic bath. Then for about five minutes the heat is made very sharp, that the whole charge may become fluid, and the mechanically mixed particles of lead may fall to the bottom.

The cups may now be removed from the muffle one by one, and their contents poured into a series of hollows in an iron plate which has been prepared for the purpose. After cooling, the lead with the silver, and if they are present, the gold and some of the copper will be found in the form of a large button at the bottom, while a dark glassy slag occupies the surface. The button is readily separated from the slag, and is now ready to be carried to the second part of the process, the *cupelling*.

Several other plans for producing the argentiferous button are more or less in use. These consist in fusing the ore with litharge, saltpetre, various reducing fluxes, or iron. The same object is attained by following the course that is in use in the assay of lead, and in many instances the two metals are determined from one

specimen, the lead button obtained by the method detailed in the section treating of the assaying of lead being weighed, and then cupelled in the manner now to be described.

THE CUPELLATION OF ARGENTIFEROUS LEAD.

The argentiferous lead, procured by *scorification*, or by any of the above-mentioned plans that the assayer may prefer to adopt, or the result of operations in the furnace upon a large scale, is now passed to the operation known as cupelling, in which the lead and other impurities are driven off, and the silver obtained in a purified form, suitable for weighing.

Lead and bismuth are the only metals that possess the property of forming an oxide, when heated in the air, that becomes fluid at a comparatively low temperature, and is then readily absorbed by a porous substance upon which they may be melted. They have further the property of dissolving more refractory oxides that may be present, and carrying them also into the porous support, leaving the less oxidisable metals isolated upon the surface.

CUPELS.

The porous support upon which the fusion and oxidation takes place is known as a *cupel*. Many porous substances have the qualities necessary for forming them, but bone ash and wood ash are principally in use, either alone or mixed with each other. In Freiberg they are formed of one part of bone ash, four parts of wood ashes, and one part of lime. The materials in the condition of a powder are mixed with

the proper amount of water, and moulded in a form to the desired shape, which is that shown in the accompanying cut. The size of this cupel should be regulated by the quantity of oxide to be absorbed, it being generally assumed that the material of which it is formed will take up double its weight of lead.

MANIPULATION IN CUPELLING.

The process of cupelling may be accomplished in a furnace such as has been mentioned above, the conditions necessary being a high temperature, and a draught of air that can be regulated at the will of the attendant, passing over the surface of the fused metal. I have seen in some establishments the flue between the chamber of the furnace and the chimney, in a common wind furnace, used for the purpose with good results.

In some laboratories a furnace such as is shown in the accompanying figures is in use. Fig. 4 represents an elevation, and fig. 5 a vertical section. The exterior is formed of strong wrought-iron plate, and the interior, where exposed to the fire, is lined with fire-brick. The muffle *m* is a small D-shaped retort of refractory clay, closed at the hinder end, open towards the front, and provided with a number of openings at the side to permit the passage of air. This muffle is heated by surrounding it with a strong fire of charcoal or coke, and for the introduction of this fuel the apertures *a* and *b* are provided.

The well-heated cupels are arranged near the middle portions of the glowing muffle, and the lead buttons to be operated upon carefully laid in them by means of a

pair of long tongs. When the metal has fused, and the litharge forms and begins to be taken up by the

cupel, the temperature is lowered as much as possible without discontinuing the operation of oxidation and absorption. The silver gradually concentrates itself in a globule in the centre of the cupel, and as it becomes purer the fire should be made sharper. The instant at which the last particle of lead leaves the silver, is marked by a beautiful phenomenon which is known among assayers as the *brightening* or *coruscation*. The globule is suddenly animated with a brilliant play of

rainbow colours. Streak after streak shoots across its surface, and the whole mass seems to be in a state of rapid rotation. This soon discontinues, the white brilliant silver grain becomes motionless, and the operation is complete. The cupel must now be cooled with care, to prevent, if possible, what is called *vegetating* or *sprouting* of the silver (see p. 27), which may result in an important loss.

After the globule has cooled it should be raised from the cupel with a pair of strong pincers, flattened by the same instrument, carefully cleaned of all foreign particles, and weighed on an extremely delicate balance. In cases where commercial transactions depend upon the result of an assay, it is always advisable to make several tests of the same sample, to guard against any accidental error.

The weight obtained upon the balance does not correspond exactly with the weight of silver contained in the sample of ore taken, a portion of the metal being always absorbed by the cupel with the oxide of lead, or volatilised. This minute loss has been found under similar circumstances to be quite constant, and in large works on assaying, tables giving the amount to be added in various cases will be found, but in practice these are frequently neglected.

In Freiberg one man can attend to the fusing and cupelling of fifty assays, in a day of eight hours, using the system described in the foregoing pages.

II.—ASSAY OF THE ALLOYS OF SILVER.

Under this head come all coins and bullion holding silver, argentiferous amalgam, rich lead, the copper

resulting from working argentiferous ores, &c., &c. The system to be pursued in their examination is similar to that given for ores; but sometimes the first process, or scorification, can be dispensed with, and the determination made at one operation.

For *compounds of silver and lead*, where the former metal exists only in minute quantities, as is often the case with the products formed in the course of Pattinson's process (see p. 146), a large sample is weighed out and slagged, as above, upon the fusing cups until small enough to be placed upon the cupel, when it is cupelled in the usual manner.

Amalgam should be very slowly heated until all the mercury evaporates, and then cupelled (upon the same cupel) with six or eight times its weight of lead.

The alloy of silver and copper is, however, the most frequently brought to the notice of the assayer in the form of coins.

The Assay of Coins by the dry way.

To determine the proportion of silver in these valuable compounds, the wet way is now usually resorted to; but a skilful assayer can obtain very accurate results in the furnace. For a proper accomplishment of the assay, a preliminary and approximate knowledge of the proportion in which copper exists in the alloy is required. The readiest means for attaining this is with the *touchstone*, which is a smooth piece of black basalt or silicious slate, upon which the colour of the streak formed by various alloys can be compared. The assayer must provide himself with a set of alloys of known composition, and when it is necessary to test an unknown compound, the streak that it

produces on the stone is compared with those made by the alloys of known composition, and the two streaks nearest resembling each other are assumed to be made by compounds with the same proportions of silver and copper. This means of trial is not exact, and may be put quite at fault by the presence of arsenic, nickel, or zinc, but it generally furnishes sufficient data to enable the charge to be made with judgment.

The quantity of lead added is apportioned to the per centage of copper present, according to the following Table :—

Silver.		Copper.	
When the alloy consists of	0.90	and 0.10	7 times the weight of alloy taken.
	0.80	„ 0.20	10 „ „
	0.70	„ 0.30	12 „ „
	0.60	„ 0.40	14 „ „
	0.01 to 0.50	„ 0.50 to .99	16 to 17 „ „

The alloy is weighed out to the amount of from 12 to 20 grains, placed in a small bone-ash cupel, with the proper quantity of lead, and cupelled with care, and the resulting globule of silver is treated as in the case of the assay of ores. When several results thus obtained do not differ more than $\frac{1}{40}$ or $\frac{1}{50}$ of a grain, the mean of all the assays may be taken to determine the quantity of silver in the alloy.

III.—DETERMINATION OF SILVER WITH THE BLOWPIPE.

This method, which is of comparatively recent invention, offers, in skilful hands, a more economical and expeditious means of determining the value of an ore or product than any other. A careful and practised operator may depend upon his results to within $\frac{1}{100}$ th of a per cent. It is of great value in making rapid

observations for regulating the working of a furnace or dressing establishment, for making the preliminary observations in the assay by the wet way; and especially in a new country, where laboratories and furnaces do not exist, it offers a resource to the explorer not to be found elsewhere.

The lamp, blowpipe, and other instruments, and the fluxes that are required, are those generally used in blowpipe experiments, and have been described in "The Rudimentary Treatise on the Metallurgy of Copper." The other articles that must be used in the assay will be mentioned in the course of the following description.

The ore from which the assay is to be taken must be ground to an extremely fine powder, and well mixed, so that a good average sample may be obtained. This, after being dried at 212° , is weighed upon an extremely delicate balance, 10 decigrammes being used for each assay. This amount is thrown into a spoon-shaped scoop, and mixed with 50 to 100 per cent. of powdered borax glass, according to the fusibility of the sample; and in proportion to the quantity of copper and nickel present, from five to fifteen times the weight of the ore of pure test lead. These substances are then poured carefully into a small capsule, made by rolling into the shape of a cylinder a bit of paper that has been soaked in a solution of the carbonate of soda, and afterwards dried.

The package thus formed is placed carefully in a hole about half an inch deep that has been bored in a firm piece of charcoal, or in a piece of artificial coal made of charcoal powder and a solution of starch, and the first fusion may now be entered upon.

The package of ore and flux is treated with a reduc-

ing flame, and the mixture fused at the same time that the paper is burned away. The earthy particles are thus slagged off, the volatile constituents driven away, and all the particles of lead brought into a single globule. During this operation, the position of the instruments should be as in the accompanying cut, in

Fig 6

which *a* is the point of the blowpipe, *b* the cavity in the coal, *c* the ball of slag, and *d* the globule of argentiferous lead. When all the lead has been collected in a single globule, and the slag is quite fluid, the reducing is changed for an oxidising flame, which

is directed only upon the lead. Signs of an internal motion or boiling soon begin to be exhibited, upon which the assayer should cease blowing, and allow the coal and contents to cool ready for the next operation.

Cupelling with the Blowpipe.

The globule of argentiferous lead is now broken from the slag by beating it between layers of thick paper.

Fig 7

8

9

The lead is pounded upon a small anvil to a cube, and is now ready for cupelling. This is done upon a small cupel composed of finely powdered bone-ash, and made by beating a portion of the powder into the hollow of a steel cup (figs. 8 and 9), by means of a smooth steel form (fig. 7). A shallow porous cup is thus formed which, for the sake of convenience in holding, is placed in a stand, such as is shown at *a*, fig. 10.

The fresh cupel is first well heated in the flame, and then the lead cube brought carefully upon it, and a good oxidising flame applied. The position of the flame and instruments may be observed in the accompanying figure, in which *b* represents the point of the blowpipe, *c* the lamp, and *d* a section of the cupel with the globule of lead upon it.

When the lead has been oxidised away until the grain of metal that remains is about as large as a mustard-seed, the cupel is allowed to cool. The globule is then cleaned of the impurities that surround it by a light blow with the hammer.

The *second period of the cupelling* requires more care than the first. A cupel should be formed in the manner above described, and with a surface as smooth as possible. The same cupel that has answered for the first fusion may often be used, after giving it a new surface of fine bone-ash. The globule of argentiferous lead is carefully deposited in the hollow of the cupel, a strong oxidation flame thrown upon the surface of the ash close to the lead, that it may be kept continually in a condition to absorb the litharge, and the globule maintained fluid without being brought directly under the flame. A few seconds before the silver becomes free from lead, a brilliant play of colours usually appears upon the surface of the fluid metal, and then the globule be-

comes white and bright. When this condition is observed, the cupel should be gradually taken from the flame and allowed to cool. The globule of silver is then taken from its surface with a pair of pincers, brushed of impurities, and weighed upon an exceedingly fine balance. From the result thus obtained, the per centage of silver in the sample may be calculated as in other assays by the dry way.

Means of determining the weight by measuring the diameter of the silver globule.

It sometimes happens that the silver globule which is produced in the assay of poor ores before the blow-pipe is so small that it cannot be weighed. To extend the usefulness of the instrument to cases of this nature, Harkort contrived a scale for the purpose of measuring the diameter of the globule, which is sufficient to determine its weight, since the weights of metallic spheres are to each other as the cube of their diameter. For this purpose he used a tablet of ivory upon which two fine diverging lines were drawn. At one end these lines intersect, at the other they are about $\frac{1}{32}$ of an inch apart. If now a globule, of less than this diameter be moved between the lines towards the point of their intersection, it will at length arrive at a spot where its exterior points, when observed through a glass, are exactly over the two converging lines. The weight corresponding to a globule of this size is marked on the edges of the scale, and can be read off directly. By this ingenious contrivance a practised eye, aided by a glass, may determine weights smaller than one milligramme to an accuracy reaching $\frac{1}{70}$ of a milligramme, or even less.

METHOD OF EXPRESSING THE QUANTITY OF SILVER
IN A GIVEN ORE.

In England and in the United States, for commercial purposes, the richness of an ore or mineral is expressed by giving the number of ounces, penny-weights, and grains troy, of silver contained in a ton avoirdupois—the standard of unity. For purposes of calculation it will be well to remember that a pound avoirdupois contains 7000 grains troy, and that the ton usually employed contains 2240 such pounds.

For convenience of reference a Table is added showing the weight of silver in the ton of ore corresponding to the weight in grains, obtained from 100 grains of mineral.

If 100 grains of ore give of fine metal	One ton of ore will yield			If 100 grains of ore give of fine metal	One ton of ore will yield		
grains.	oz.	dwt.	gr.	grains.	oz.	dwt.	gr.
·001	0	6	12	·280	91	9	8
·010	3	5	8	·290	94	14	6
·020	6	10	16	·300	98	0	0
·030	9	16	0	·310	101	5	8
·040	13	1	8	·320	104	10	0
·050	16	6	16	·330	107	16	0
·060	19	12	0	·340	111	1	8
·070	22	17	8	·350	114	6	8
·080	26	2	16	·360	117	12	0
·090	29	8	0	·370	120	17	2
·100	32	13	8	·380	124	2	16
·110	35	18	6	·390	127	8	0
·120	39	4	0	·400	130	13	8
·130	42	9	8	·410	133	18	6
·140	45	14	16	·420	137	4	0
·150	49	0	0	·430	140	9	8
·160	52	5	8	·440	143	14	16
·170	55	10	16	·450	147	0	0
·180	58	16	0	·460	150	5	8
·190	62	1	8	·470	153	10	16
·200	65	6	16	·480	156	16	0
·210	68	12	0	·490	160	1	8
·220	71	17	8	·500	163	6	16
·230	75	2	16	1·000	326	13	8
·240	78	8	0	1·500	490	00	00
·250	81	13	8	2·000	653	6	16
·260	84	18	6	2·500	816	13	8
·270	88	4	0	3·000	980	0	0

The inconvenience of this plan of expressing the richness of a silver ore or product often occurs to practical men. Like our entire system of weights and measures, it requires a radical revision. The most enlightened nations of the Continent have adopted methods by which the expression may always take a decimal form. In France, the quantity of silver is given by stating the number of grammes in a hundred kilogrammes, or in $\frac{1}{100000}$ ths. In the Hartz, the old system of weights has been thrown aside; 100 pounds is assumed as the standard of unity, and the value of argentiferous minerals is given in *quint*, or in $\frac{1}{10000}$ ths. In Saxony a no less convenient system has superseded the old method of reckoning by *loth* and *mark*; the richness of their silver ores is expressed in *Pfundtheile*, one of which is equal to $\frac{1}{10000}$ th of 100 pounds, which quantity is taken as the standard of unity, and contains, according to law, 50 kilogrammes.

THE SEPARATION OF SILVER AND GOLD.

If an ore or product containing both silver and gold be treated according to the method heretofore described for the assay of silver, the globule that is found on the cupel after the conclusion of the operation will contain not only the silver that existed in the sample, but also the gold. It becomes necessary here to separate the two metals, that the quantity of either present may be known.

Inquartation.

Gold will not dissolve in nitric acid, but silver, pure or in all its compounds with gold, to a point where the gold does not exceed about one-fourth of the mass, is attacked by that acid, and the silver converted into a

soluble nitrate, while the gold remains behind. If too much silver be present, the gold remaining after the operation will be in the form of a fine powder that is difficult to collect. Hence the assayer strives to produce a compound having about three parts of silver to one part of gold (or from 70 to 80 per cent. of silver), by adding, when the proper proportion does not already exist, a weighed quantity of the former or the latter metal. To know the amount of either that should be added, he is compelled to make preliminary estimations, for which a careful trial upon the touchstone will be found sufficient. The gold remaining after the solution of the silver is weighed; the difference between this and the weight of the original globule, after deduction is made for any gold that may have been added, will give the quantity of silver that has been dissolved.

II. "THE ASSAY OF ARGENTIFEROUS COMPOUNDS BY THE WET WAY."

The difficulty of obtaining results of a perfectly reliable character in determinations of silver by the dry way, has caused the introduction into many of the European mints of what is known as the method of Gay-Lussac.

This plan is generally in use for the determination of the value of alloys, and the presence of no metal, except mercury, seems to injure the precision of the results that may be obtained by its means.

The assay is performed by dissolving the argentiferous compound in pure nitric acid, and then, by means of a solution of chloride of sodium (common salt), graduated to such a strength that a determined

quantity will precipitate a determined weight of silver, all the silver is thrown down as a chloride. It is evident, that if just as much of the standard solution of the chloride of sodium is used as is sufficient to precipitate all the silver, and the amount of the solution added has been measured, the amount of silver present can be readily reckoned.

This method, besides its admirable accuracy, is recommended by the quickness with which determinations may be made by it. In a well-arranged laboratory, thirty assays may be made in a day, if the alloys have already been weighed out, and their richness is approximately known.

CHAPTER VIII.

THE ASSAYING OF LEAD ORES AND OTHER PLUMBIFEROUS COMPOUNDS.

THE comparatively low temperature at which lead volatilises, the difficulty with which it can be obtained free from copper, zinc, arsenic, and antimony, and its disposition to go over into the slag in the crucible, renders this assay one of the least satisfactory that the metallurgist is frequently called upon to perform. Although recourse has been had to the wet way in the search for a rapid and accurate method of determination, this desideratum is still unsupplied. By proper precautions, however, the methods now in use may be made to yield results that are extremely valuable in practice, and, where the ore or product is rich, those that differ but slightly from absolute truth.

It is usual to perform the assay of lead by two methods, depending in their nature upon the character of the sample of ore.

In the *first* division fall ores and products of lead containing neither sulphur nor arsenic, or those substances only in small proportions. This class of compounds is among the ores comparatively unimportant.

The *second* division embraces those ores and products with which sulphur or selenium are combined.

THE ASSAY OF OXIDISED PLUMBIFEROUS SUBSTANCES.

The phosphate, the arseniate, and the chromate of lead may be assayed by charging the crucible with 100 to 200 grains of the mineral, and adding three to four times the weight of carbonate of potash, and 20 to 30 per cent. of powdered coal. Upon the top of these a heavy layer of common salt must be added, to prevent the action of the air, and the whole fused by a gradually increasing temperature. The button of lead formed in the bottom of the crucible may be taken out by breaking the vessel, cleaned of its enclosing slag, weighed, and the per centage of metal calculated at once.

The *Carbonate of Lead*, *Litharge*, and the various *Abstrichs* may be easily tested by fusion with the above reducing charge. If, however, in any case sulphur is supposed to be present, a small quantity (from 5 to 10 per cent.) of iron should be added.

THE ASSAY OF PRODUCTS POOR IN LEAD.

Although only capable of giving a moderately accurate result, the following charge has been found valuable for assaying poor slags in making determinations for controlling the working of a furnace. To the powdered

mineral is added three or four times its weight of black flux, consisting of one part of saltpetre and two parts of crude tartar, which have been mixed intimately and deflagrated, 20 to 40 per cent. of borax, and 5 to 10 per cent. of iron. To this mixture, for the better collection of the lead, a small and weighed quantity of silver is added.

The silver and lead are found together at the end of the operation, and the excess of the weight of the button of alloy obtained, above the weight of silver added, will express the weight of lead in the sample.

THE ASSAY OF PLUMBIFEROUS SUBSTANCES CONTAINING SULPHUR.

Several methods for assaying this class of ores are employed at metallurgic establishments. The best are those that are carried out with the use of *metallic iron*, which acts the part of a precipitant for the lead by combining with the sulphur, a *carbonated alkali*, as soda or potash, which serves to confirm a fluid slag and assists in reducing the lead, and a quantity of *carbon*, as coal powder, or in the form of black flux. This last addition answers to reduce the alkali, forming potassium or sodium, which in its turn combines with the sulphur, and is also valuable for preventing the injurious access of the atmosphere to the assay.

When this plan of assaying is properly managed, it will produce 84.85 per cent. of lead from pure galena, which is within 1.70 per cent. of the entire amount present.

Two species of this assay are recognised, the first of which is carried out in a clay crucible, the second in a crucible of wrought iron.

Assay in a crucible of refractory clay.

This method is recommended by many assayers as superior to all others. It is sufficiently accurate, quickly performed, and cheap.

A crucible is used similar in form to that shown in fig. 11, which may be $4\frac{1}{2}$ " high and $1\frac{7}{8}$ " greatest interior diameter. The bottom is broken off after the crucible has been used, and serves to form a cover during subsequent assays, being used in the manner shown at *b*. The powdered ore is weighed out and placed in the bottom of the crucible. About 60 grains is a charge adapted to a vessel of the size given above; when much more is taken, one of larger dimensions is required. Upon the powdered ore 10 to 30 per cent. of iron is placed. The iron should not be added in the form of filings or scraps, as some assayers recommend, since the small pieces, if they remain undecomposed, may be difficult to separate from the metallic lead. The quantity of iron added between the above-mentioned extremes must depend upon the amount of sulphur combined with the lead. If pure galena is treated, 22.6 per cent. will exactly enter into combination with all the sulphur; but it is always better to use too much than too little.

Upon the ore and iron, black flux to the amount of three times the weight of the ore should be thrown, or what will answer the same purpose, a mixture of potash with wheat or rye-meal in the proportion of 100 of the former to 18 of the latter. A spoonful of common salt is placed above these substances as a protection against the air, and a small piece of charcoal thrown in on the top.

The crucibles, after having been covered in the

manner shown in fig. 11, may now be introduced into the furnace, and raised by degrees to a strong red heat, at which temperature they should be kept for about half an hour. They may then be removed from the fire, given a slight blow to settle all the metallic particles to the bottom, and set aside to cool. Upon breaking the crucible the lead should be found in the form of a well-defined button attached to the undecomposed iron. A few blows with a hammer directed upon the iron will serve to divide the two, and the lead may be weighed at once.

When a large quantity of the sulphides of iron, zinc, or copper are present in the ore, a roasting should be performed previous to the application of the above plan, and a small quantity of glass powder or borax added in the charge.

Assay in a crucible of wrought iron.

By this plan the iron for precipitation, instead of being added, as in the foregoing, as a separate piece among the fluxes, is supplied by the sides of the crucible.

In North Wales* the rich galenas are assayed after decrepitating in a separate vessel by heating them strongly, without the addition of fluxes, in a dish or ladle of iron. The lead is reduced to a metallic form and poured into a mould of cast iron; the sulphide of iron and slags that remain in the dish are heated again, to clean them as much as possible; the lead produced is added to the large button in the iron mould, and the two are then weighed. This extremely simple plan is

* Phillips' Manual of Metallurgy, p. 475.

said to give as much as 79 to 83 per cent. from pure galena, but it cannot be employed for poorer ores without danger of serious loss.

I have met with the following method in use at several large establishments where the ores had, beside the sulphides of lead and the usual earthy impurities an admixture of zinc and iron, with occasionally a little copper.

Wrought iron crucibles having the shape shown in the accompanying cut (fig. 12), are in use. They are formed by bending a thick plate around a mandril, welding the edges together, and then attaching a thick bottom, also by welding.

The flux consists of 3 parts of tartar 2 parts of saltpetre, 1 part of borax, and 6 of soda, all of which are finely powdered and well mixed.

The furnace in use is similar to that shown in fig. 13, the chimney being at least 30 feet high, to insure a good draught.

In performing the assay a crucible is placed on the fire and allowed to grow hot; the ore, which has been previously weighed out to the amount of 300 grains, is mixed with two large spoonfuls of the flux, and thrown into the hot crucible. In from five to eight minutes

Furnace.

the charge should be in a complete state of fusion. The assay is then poured into a mould of iron, formed as

is shown in the adjoined cut (fig. 14), with two deep conical holes for the reception of the fluid mass. The

Mould.

lead collects by reason of its high specific gravity at the bottom. It is removed by reversing the mould, broken from its accompanying slag, and weighed.

Two crucibles are often used alternately, in which case it is possible for one assayer to make 9 or 10 fusions per hour. The crucibles, when heavy and carefully welded together, will last for from 25 to 30 fusions, when their sides usually become eaten through by the sulphur.

Assay of Lead Ores by fusion with carbonate of potash.

This assay falls behind both the other methods in accuracy, and can only be recommended in the rare cases in which antimony forms a considerable constituent of the ore. It is, however, interesting as being almost the only method of assaying galena in the ancient metallurgic region of the Hartz, as the process with iron is nearly exclusively that employed in Saxony for the same purpose.

About 75 grains of mineral are carefully weighed out, mixed with 300 grains of potash, placed in a small fire-clay crucible, and covered with a layer of salt about $\frac{1}{4}$ " in thickness. This is placed in a muffle, fused, and kept at a high heat for half an hour. It is then allowed to cool with access of the air, and to remain at a brown red for ten to twenty minutes; subsequently brought

to a high temperature, and in about ten minutes taken from the furnace, allowed to cool, the button of lead which has collected at the bottom broken from its slag, and weighed.

Forty of these assays may be made at once in a single muffle furnace, but the utmost care cannot produce over 80 per cent. of lead from pure galena.

PART II.

GENERAL ARRANGEMENT. USE OF REVERBERATORY FURNACES ; USE OF CUPOLA FURNACES ; USE OF HEARTHES ; TREATMENT OF OXIDISED PRODUCTS ; SEPARATION OF SILVER FROM RICH LEAD ; TREATMENT OF SILVER ORES BY THE WET WAY ; STATISTICS.

CHAPTER IX.

GENERAL ARRANGEMENT OF THE SUBJECT—PRODUCTION OF LEAD AND RICH LEAD FROM SULPHUROUS ORES IN REVERBERATORY FURNACES.

In the following chapters I propose to give a general view of the systems in use for producing the marketable metals, silver and lead, from their ores as delivered from the miner or dresser to the hands of the smelter. The processes in this branch of metallurgy are exceedingly various, and the traveller passing from one silver or lead producing district to another, rarely fails to find in each new region methods and apparatus that he had not seen before.

The causes that influence the adoption or rejection of any particular furnace are so numerous and varying, that such differences must always be expected, and a careful consideration of the subject will generally show the unprejudiced metallurgist that, at least in old districts, where circumstances have remained the same through a long series of years, the peculiar processes of each locality are the result of a most ingenious con-

sideration of the difficulties and facilities that may influence the production of the desired metals, and further, that to introduce any radical change would be attended with much danger of pecuniary loss. Of course, in new countries, where all is, so to speak, in an experimental condition, or where the sciences of Chemistry and Natural Philosophy have presented the investigator with fresh knowledge, by which to direct the powers of nature, radical changes may often prove very beneficial. But numerous instances can be adduced to prove the justness of the above remarks, which are especially intended for that class of persons who find in the limited district with which they may be familiar, the model after which they would build all the furnaces, and work all the ores of the world.

Thus, for working the silver and lead ores of Bohemia, an attempt was made to introduce the American hearth, and extensive trials with that object in view were carried out with the utmost care; but although several advantages were promised, the attempt was abandoned, on account of the metal lost, and the difficulty and unhealthfulness of the labour. In the Hartz, an equally determined attempt was made to import the English plan of working lead ores, as practised in Flintshire, and was no less unsuccessful. A slight admixture of quartz, which is almost invariably present in the ores of that region, prevented a complete extraction of the metal, and the old plan of working in cupola furnaces, and precipitation with iron, was returned to and is still practised.

The numerous efforts that have been made to introduce the European system of amalgamation into the South American and Mexican works, have but in a

comparatively few cases been attended with success, the American system, which grew up in the new hemisphere, being found, notwithstanding its wastefulness of quicksilver, to be best adapted for all the circumstances of that region.

The influences most important in modifying the character of the metallurgic processes adopted in different localities, are to be sought in the *nature* and *richness* of the mineral furnishing the metal; the *species of earthy gangue* with which it may be accompanied; the *absolute* and *relative* price of various fuels, and the *nature of the flux* that may be abundant in the vicinity; to which may be added, the metallurgic traditions of the country.

In studying the processes in the smelting of silver and lead, which these varying influences have made so numerous, the following division will be adopted.

- I. *The Production of Lead and Rich Lead from Sulphurous ores and products.*
- II. *The Production of Lead and Rich Lead from Oxidised ores and products.*
- III. *The separation of Silver from Rich Lead.*
- IV. *The working of Silver ores or products non-plumbiferous.*

We have seen in the sketch of the history of silver and lead, that from the most remote periods, the metallurgy of the two metals has been very intimately connected. This has not been simply a consequence of their almost invariable occurrence together in nature. Certain properties appertaining to both metals made lead, until the discovery of the process of amalgamation, an essential substance in smelting all but the

very richest ores of silver. It acts the part of a solvent, to take up the disseminated particles of the metal; or, if I may be allowed the expression, it serves to *wash* the silver from its impurities, and carry it in suspension from among the mass of earthy and metallic substances with which it may have been combined or mingled. To perform this function, lead possesses properties that make it superior to all other metals; and hence, where it does not exist in sufficient quantities in the silver ore, it must be added in the course of the process.

Among these properties, the following are the most important:—

1. When lead is fused with sulphide of silver, that compound is decomposed, sulphide of lead is produced, and silver is liberated in a metallic condition.

2. When oxide or sulphate of lead is fused with sulphide of silver, the sulphur passes off as sulphurous acid gas, and argentiferous lead is the result.

3. When metallic lead is fused with the oxide or the sulphate of silver, the silver is set free and combines with the lead, while the oxide of lead is produced in the first case, and oxide of lead and sulphurous acid in the other.

4. Lead readily alloys itself with silver, but exhibits much less affinity for the baser metals with which silver is usually mingled.

5. When lead containing silver is subjected while in a fused condition to the action of a blast of air, the lead will be oxidised, while the silver remains unchanged.

These properties of lead and its compounds, combined with those mentioned at pages 46 and 47, allow simple means to be taken—

- 1st. To form from the very impure mineral the com-

paratively concentrated argentiferous alloy, or *Rich lead*.

2nd. To separate the two metals forming this intermediary alloy, and thus attain the grand end of obtaining both metals in an isolated condition.

The efforts of the furnace man are *first* directed to the production of the *rich lead*, for which purpose three systems are in general use. These may be distinguished by the construction of the furnace employed, as follows:—

A. *Reduction of Ores in Reverberatory furnaces.*

B. *Reduction of Ores in Cupola furnaces.*

C. *Reduction of Ores in Hearths.*

A.—THE REDUCTION AS CARRIED OUT IN REVERBERATORY FURNACES.

The reduction of lead in reverberatory furnaces is accomplished either by what is known as the treatment by *double decomposition*, or by *reactions*, in which the greater part of the lead is obtained from the ore without the use of a flux, but simply by the aid of oxygen introduced from the atmosphere; or, *secondly*, by treatment with iron, when the reactions mentioned at page 46 take place, and metallic lead is produced. The first method is adapted for rich ores, with baryta, lime, and blende in small quantities among the impurities, and is by far the more important of the two systems. The second has been sometimes used for working ores containing much quartz and clay.

Among the advantages secured by working ores in the reverberatory furnace, may be mentioned the use that can be made of unprepared fuel, the control possessed by the workman over the action of his

furnace ; the fact that but a comparatively small portion of slag remains after the operation ; and further, the circumstance that no blast is needed, and usually no expensive flux is required.

In general, in the treatment of ores in a reverberatory furnace, three periods may be distinguished. *In the first* a roasting is accomplished, with access of air, until the contents of the furnace have come to consist of oxide and sulphate of lead and undecomposed sulphide. *In the second* period these are made, by raising the temperature, to react upon each other, so that metallic lead is produced ; and *thirdly*, the furnace-man endeavours to draw still more lead from the half-fused charge by treating it with lime or with coal. The residue of the operation is generally taken from the hearth, and treated for the remainder of its metal, usually in a blast furnace.

According to the length of time required for the roasting, and the temperature employed to accomplish it, the relative amount of oxide and sulphate of lead will be various, and hence, in the second period of the process, the reactions will be different. This gives rise to three systems of smelting in reverberatory furnaces, known respectively by the countries in which they are chiefly employed, as *the English process*, *the French process*, and *the Carinthia process*.

THE ENGLISH METHOD OF SMELTING SULPHUROUS ORES IN THE REVERBERATORY FURNACE.

When the sulphide of lead is roasted a short time by a rapidly increasing heat, there is a certain amount of sulphate of lead produced, and much sulphide of lead

remains undecomposed. If now the charge be quickly raised to a very high temperature, there will be a mutual decomposition of the contents of the charge, and *lead*, the *sub-sulphide of lead*, and *sulphurous acid* will be formed. Thus:—

The subsulphide of lead has the peculiarity, when allowed to cool slowly, of setting free a portion of its lead, and forming a higher and less fusible compound with sulphur. In order to free this lead, the charge is cooled by opening the doors of the furnace. This is followed by another heating. The change of temperature is thus repeated several times, and in order that the charge may not fuse too easily, and may be kept spongy, so that the various reactions may go forward, and further, that it may combine with the sulphuric and silicic acids, some powdered lime is added; and at the same time a small amount of charcoal, to act as a reducing agent. When the lead ceases to flow from the tap-hole, the slags that remain in the furnace are drawn out into a trough filled with water, and since a considerable portion of valuable metal still remains mingled and combined with the earthy substances, they are subjected to a subsequent treatment in a peculiar apparatus, called a *slag-hearth*, or cupola furnace, which will be found figured and described in a subsequent Chapter.

This system of treating sulphurous ores has proved itself very well adapted for many English minerals

which contain a small quantity of lime; if however quartz, even to the amount of three or four per cent., or a small portion of the sulphide of antimony be present, the early part of the process will be attended by a disadvantageous clotting of the charge.

THE REVERBERATORY FURNACE.

There exist several modifications of this apparatus. The usual construction of those employed in the north may be understood from the accompanying horizontal and vertical sections (Figs. 15 and 16). Like all reverberatory furnaces, it consists of three essential parts; the fireplace, the hearth, and the chimney.

The *hearth* *a* is hollow or funnel-shaped, so that a fluid substance placed upon it will run by its own gravity into the lowermost point at *p*. This hearth or bottom is formed of a layer of fire-bricks *b*, upon which rests a thick bed of vitrified slags, which is formed by bringing the slags into the furnace, closing the doors, and raising the temperature until they take on a semi-fluid condition, and then working them with rakes and paddles into the proper form.

The doors *k k k* are six in number, three on each side. They form apertures, through which the charge may be worked, and its temperature regulated; they are capable of being tightly closed when necessary. The inclination of the hearth is more rapid in the vicinity of the *fire-bridge c* than toward the chimney, in order that the metal may not be too long exposed to the oxidising and volatilising influences of

a current of strongly heated air. The molten metal collecting in the hollow at *p* can be drawn out through a hole into the exterior iron basin *l*. This *tap-hole*, when not in use, is closed by a pellet of clay.

The grate *e* is composed of strong iron bars, and is supplied with fuel through the door *n*, which opens upon the side of the furnace known as the *labourer's side*, in contra-distinction to that upon which the cistern *l* is placed, which is known as the *working side*. The charge, which is sometimes subjected to a previous roasting, when the ores are poor or much mixed with pyrites, is either introduced into the furnace through the side doors, or by means of the hopper *m*, which being placed above the hearth, is filled with ore, and

at the proper time by drawing out a slide at its lower extremity, the necessary quantity is projected at once into the furnace. The *arch b* gradually declines from the fire-bridge *c* to the opposite end of the hearth. Through the aperture the fumes and products of combustion pass into the flue *h*, and hence are carried through the proper condensers to the chimney. The draught may be regulated by means of the damper *i*, which may be raised and lowered at the will of the attendant. The charge employed in this furnace varies in amount at almost every establishment. In Newcastle and the neighbourhood, it is from 12 cwt. to 14 cwt.; near Bristol, 21 cwt.; while in Cornwall charges of 30 cwt. are not unfrequently worked; and, according to the weight and nature of the ores, the time required for smelting a charge, varies between six and twenty-four hours.

The size of the furnace must differ largely in the various districts; but in the north in general the grate *e* is 5 ft. 9 in. $\times$ 1 ft. 10 in.; the thickness of the fire-bridge *c* is 1 ft. 6 in.; the length of the sole is 9 ft., and its average width is 7 ft; the height of the roof at the fire end 1 ft. 3 in., and at the end toward the flue, it descends to about 11 inches.

THE CARINTHIA PROCESS OF SMELTING SULPHUROUS ORES IN THE REVERBERATORY FURNACE.

Where galena is roasted by a slow and gradually increasing temperature, a point is at last reached where the charge contains, besides some oxide, the sulphate and the sulphide of lead in the proportions of the weight of their respective atoms.

If the temperature be now raised, and the charge vigorously stirred, the following reactions will take place :

At the same time some sulphide of lead is formed, which, when subjected to the action of the sulphate, metallic lead is produced as follows :—

As the roasting pushes the decomposition of the galena still further, a point is at last reached, where for one equivalent of sulphide, three equivalents of sulphate are present. Then by mutual action there is no longer a production of metallic lead, but of sulphurous acid, and oxide of lead or litharge, thus :—

When now charcoal is added to the mass, the litharge and sulphate of lead are reduced, and more metallic lead is obtained.

Upon these reactions is founded what is known as the Carinthia process, which is largely employed in the province of Austria of that name, in the neighbourhood of Bleiberg. The ores require to be of the purest character. Those treated at Bleiberg do not contain sufficient silver to pay for the trouble of extracting it,

but the same method has been employed in Nassau for working argentiferous ores, and a plan, but slightly differing from, is in use for galena poor in silver, in the southern part of Spain.

The Furnace employed in Carinthia.

The reverberatory furnace in which the lead of Carinthia is smelted, differs essentially from that in

use in England, as the accompanying cuts will show. Fig. 17 represents a front elevation, Fig. 18 a horizon-

tal section along the line A B of Fig. 19, Fig. 19 a vertical section along the line C D, and Fig. 20 a vertical along the line E F.

Two furnaces are usually placed side by side, as is indicated in the drawing, one chimney answering for both. The hearth of these furnaces, instead of being broad and hollowed, with a tap-hole at the side, as in England, is narrow, and is furnished with a regular slope from the fire end to the flue, and is so arranged that a fluid substance will flow from any part of the furnace into the exterior trough *a*. This hearth is formed of two concentric beds *c* and *d*, each about 6 inches thick, the lower being composed of beaten clay, the upper of slags, produced in the course of the process of fusion. Its length is about 1 ft. 6 in.,

its breadth, 5 ft., and inclination about 1 in 6. The arch C is curved like the sole, but in an opposite direction, and at its point of greatest elevation, the two are about 23 inches apart. The working door *g* is 1 ft. 6 in. high, and is supplied at its lower part with a cast-iron plate, which advances over the basin *a*, forming a spout. The fire-place is indicated by the dotted lines *ppp* in Fig. 18, and is shown in the section Fig. 20. It is 1' 6" by $4\frac{1}{2}$ ft., and the grate is formed of stone. The products of combustion after passing over the contents of the hearth are allowed to escape through the flue immediately above the working door, and they thence pass to the chimney *h*, which is 26 feet high. The fuel employed is entirely the wood of the spruce and pine. The charge, which is usually about 420 pounds of galena, is thrown into the furnace through the door. The working of a charge ordinarily requires twenty-three hours, and where the mineral yields 65 per cent. of lead by assay, about 60 per cent. is extracted. The slags produced are carefully examined for lead, and when rich, are sent to be washed, and are treated again, while the remainder are laid aside for making the hearths. The lead produced flows into the exterior basin, is purified by a second fusion, and then cast into pigs. Two furnaces require the attention of eight workmen, six of which remain at the furnace during a period of twenty-four hours, and afterwards rest for two days. The wages of each of these chief workmen amounts to about 19*l.* per year.

A furnace with two reverberatories will consume annually about 480 tons of wood, working up 300 tons of ore, and producing 180 tons of lead.

Recently an improvement has been introduced into the above described furnace. Two hearths are placed one above the other, and the earlier part of the process carried out above, and the treatment finished below. This is said to produce a notable economy in fuel, and in the amount of lead lost.

THE FRENCH METHOD OF SMELTING SULPHUROUS ORES IN REVERBERATORY FURNACES.

When galena is subjected to a protracted roasting in a slowly increasing temperature, at length a large portion of ore takes on the form of sulphate of lead, a smaller that of oxide lead, and some sulphide remains undecomposed. If now the process be interrupted, and the temperature raised, without bringing the charge to a state of fusion, these compounds so react upon each other that sulphurous acid, metallic lead, and oxide of lead are formed, which last may then be reduced by treating it with coal, and metallic lead will be the result, as has been described when speaking of the Carinthia process.

Upon these reactions rest the process which is known as the French method of smelting lead in reverberatory furnaces.

The French reverberatory furnace.

The furnace used in carrying out this system of smelting, differs materially from that employed in England, although similar in having a hearth inclined toward a side aperture, which serves for tapping off the fused metal. It is, however, generally somewhat

smaller and proportionally narrower. Figures 21, 22, and 23 will serve to explain the general form and construction; Fig. 21 being a vertical section through

the middle of the apparatus, 22 a horizontal section along the line C D, and Fig. 23 a traverse section along the line E F. The furnace is supplied with three doors, all on the same side, and close together. Before the middle one is the exterior basin B, into which the contents of the hearth may be tapped. The

chief dimensions of this apparatus are as follows:—
The grate *b* is 20 in. by 4 ft. 4 in. The fire-bridge *d*

is 23 in. wide, the hearth *e* 11 ft. by 6 ft. 3 in. It is formed of a mass of tenacious clay resting upon a vault of granite. When carefully constructed and well beaten down, it soon becomes impregnated with materials of the ore that is fused upon it, and will then last a year without very material repairs. The arch *f*, it will be observed, corresponds in its inclination toward the side at which the tap-hole is placed, with the inclination of the hearth beneath. In Bretagne, the furnaces are constructed chiefly of heavy blocks of granite, well held together by iron rods and bearing-plates.

At Poullaouen, in the above-named province, the average quantity of lead in the ores, as shown by assay, is 66 per cent., and the silver amounts to about 11 ozs. per ton. 2,600 lbs. of this ore are treated at once, being thrown through the doors upon the hearth, and heated gradually, so that in five hours a dark red

temperature is reached. Then the doors are closed, and the charge heated until it begins to soften, when the workman stirs vigorously, and the reactions taking place, the reduced metal flows into the exterior basin. This stirring is succeeded by a second period of roasting for two hours, and a second stirring is given, which intermittent labour is continued several times. At the end of about thirteen hours the labourers throw in coal and wood, which reduce the oxide of lead, and the metal flows into the basin. A last roasting and stirring is then given, and the slags are drawn from the furnace and broken up for fusion in a cupola furnace.

The time usually necessary for treating a charge is sixteen hours, two labourers being required for each reverberatory. From 2,600 lbs. of mineral give by this treatment 1,216 lbs. of lead, containing 21 ozs. of silver per ton, and 840 lbs. of slag, containing by assay 38 to 39 per cent. of lead, and not more than 3 ozs. of silver to the ton.

The treatment of one ton of ore costs 14*s.* 6*d.* The lead is purified by stirring with beams of wood, and repeated skimmings, and is cast into moulds of iron, and passed to the cupelling furnace.

Upon account of the comparatively low temperature employed in this process, the ores are not so much disposed to clot in the roasting as in the treatment by the English method, and hence a more impure mineral may be employed. The presence of the sulphide of iron aids in the production of sulphate of lead, but increases the amount of slags. In England, a larger proportion of lead is extracted from the ores, and hence the process there in vogue is superior to that just described.

TREATMENT OF GALENA WITH IRON IN REVERBERATORY FURNACES.

This plan was at one time in use in France for the reduction of Spanish galena, whose gauge was largely quartzose. It takes advantage of the property possessed by metallic iron, when brought in contact with galena at a high temperature, to produce metallic lead and sulphide of iron, by the reactions mentioned at page 46.

A furnace, such as is shown in the accompanying vertical section, was employed. It was charged through

Fig 24-

a lateral door with 800 pounds of galena in the form of a powder, and holding about 80 per cent. of lead. This was mixed with 200 to 240 pounds of scrap or cast-iron, and heated rapidly until the galena began to agglomerate. Then the temperature was held stationary, and the charge stirred, that the reactions might take place. The reduced lead falls by reason of its great weight, to the lower part of the furnace at *p*, while the matt formed by the iron swims upon the surface, and a lighter slag forms the upper layer. The entire contents of the apparatus are drawn off through

the tap-hole *t* into the exterior basin. The lead remains in the basin while the slag and lead flow out upon the floor. The matt will be found to contain 5 to 12 per cent. of lead, and 4 to 5 per cent. of the same metal will remain the scoriæ, while about 4 per cent. of the metal passes off by volatilisation. The matt and scoriæ may be treated in a cupola, for their valuable metals, particularly when much silver is present, since a notably large quantity of that substance goes into the matt.

When the galena contains 80 per cent. of lead, 67 to 70 per cent. of the metal may be extracted from it by this method, which, however, is attended with too much expense for flux and fuel, to be used in large establishments where much ore is to be treated. Where but a few tons of metal are to be reduced from a galena rich in lead, and non-argentiferous, and where no other furnace is at hand, and skilful workmen cannot be obtained, it may be used with advantage.

REDUCTION WITH IRON AFTER ROASTING THE ORE.

A second system, in which iron is employed as a reducing flux in reverberatory furnaces, has been applied by Rivot and Phillips.

The furnace employed has a hearth slightly inclined toward a basin at the side, which is situated before one of the two lateral doors. The flames pass directly from the furnace to the chimney without the intervention of any condensing chambers.

The mineral, to the amount of 1600 pounds, is thrown in at one of the side doors, well spread over the hearth,

and by a moderate heat roasted for twelve hours. At the end of this time, $1\frac{1}{2}$ per cent. of charcoal, and 12 per cent. of quartz sand (if the ore does not already contain enough of that material) are thrown in, and the temperature raised rapidly to a cherry red. The charcoal acts upon the oxide forming metallic lead, and also facilitates the action of the quartz. This latter decomposes the sulphate, forming a silicate of lead. The boiling that results from this chemical action presently subsides, and iron is thrown in, and the charge stirred thoroughly. The silicate of lead is acted upon by the iron, producing metallic lead and silicate of iron. When the slags are sufficiently impoverished, the contents of the furnace are tapped into the exterior basin, which is large enough to hold all the lead, but allows the slag to flow off to the side. The lead, as in the former case, should be purified by stirring it with a stick of green wood, and, by repeated skimmings, prepared for market by a second fusion.

By this process, an ore containing 70 to 75 per cent. of lead, may be made to yield 60 to 65 per cent. of metal, the remainder being lost or volatilised in the slags.

Like the plan, the description of which immediately precedes this, the reduction of roasted ores in reverberatory furnaces, by means of iron, cannot be carried out with profit on a large scale. It may be adopted when but little ore is to be reduced, and it is not desired to erect machinery for blowing.

These two processes, where iron is employed as a precipitant in reverberatory furnaces; form a sort of connecting link between the system described in this chapter and that of producing lead, and rich lead in cupola furnaces, which we are now about to study.

CHAPTER X.

THE PRODUCTION OF LEAD AND RICH LEAD FROM SULPHUROUS ORES IN
CUPOLA FURNACES — PRODUCTION OF LEAD AND RICH LEAD IN
HEARTHES.

UPON the continent, the greater number of establishments treating argentiferous lead ores employ the cupola furnace. In England this is not the case, the reverberatory, of the form already described, being in most general use. The ores treated in cupola furnaces are usually of a more impure character than those smelted in reverberatory furnaces, the latter, as has been before remarked, being used with the greatest economy when an ore containing but little silica can be obtained.

The cupola furnace is essentially a shaft or chimney-like space, having a height greater than its breadth, in which the ores are fused while mixed with fuel, and generally by the aid of a blast.

The cupola furnaces employed in different localities, exhibit a great variety of form and dimension. These differences result sometimes from a careful consideration of the peculiarities of the ore to be treated, and an attempt to economise fuel and metal, but more frequently they appear to have originated in chance. The accompanying comparative drawings, for which I am indebted to my friend Hüttenmeister Vogel, of Joachimsthal in Bohemia, whose improvements in lead smelting are highly and justly appreciated by continental metallurgists, will show at a glance the amount

and the nature of these variations, and will at the same time give the reader a conception of the usual form of this class of apparatus.

The drawings are to a scale, and they represent with two vertical and two horizontal sections (one taken at the upper, the other at the lower part of the shaft) the form of the space between the walls of the furnace, and the examples are from six of the most important lead and silver producing districts of central Europe.

The accompanying Table gives the size of the furnace, number of tuyères, pressure of blast, quantity of air delivered per minute, and the amount of lead lost in the operation, as shown by comparing the assays of the ore with quantity of metal produced.

	Shaft from back to front.	Shaft from side to side.	Height from tuyère to funnel head.	Pressure of air.	Quantity of air per minute.	Number of tuyères.	Loss of lead per cent.
	inches.	inches.	feet.	lines of mercury.	cubic feet.		
Przibram . .	36	26	$9\frac{1}{2}$	$4\frac{1}{4}$	85	1	16
Freiberg . .	42	64	10	$1\frac{3}{4}$	157	2	9
Schemnitz . .	42	48	13	7	228	2	17
Hartz . . .	39	28	17	$7\frac{1}{2}$	353	2	...
Silesia . . .	36	28	$17\frac{1}{4}$	...	237	1	...
Joachimsthal.	50	48	$20\frac{1}{4}$	6	280	2	0.2

There are two methods in general use for smelting argentiferous lead ores or products in cupola furnaces.

- I. *The ore is fused raw, with iron or some ferruginous flux.*
- II. *The ore is previously roasted, and then fused with iron or some ferruginous flux.*

I.—THE ORE IS FUSED RAW, WITH IRON OR SOME FER-
RUGINOUS FLUX.

This method is in general use in Silesia and in the Hartz. The accompanying vertical section of a furnace employed in the former country which differs slightly from that figured before, will serve to explain the plan of constructing and operating apparatus of this character. The walls *a a* are vertical. From the tuyère upward for a distance of 10 ft. 4 in. to *b*, the section of the furnace is a rectangle, of which the sides are 3 ft. 3 in., and 3 ft., above this the section of the shaft is circular, and its diameter 3 ft. 3 in. The interior wall or *shirt a* is constructed of fire-brick, and the exterior *c c* of common brick. The charge of ore, flux, and fuel is prepared upon the floor *e*, and thrown into the furnace at *f*. Gradually fusing under the influence of the wind projected into the furnace at *t*, the desired chemical changes take place, the hearth at *h* becomes filled with fluid lead, upon which

swim the slags, that may be drawn off through the eye c, while at proper intervals the reduced metal may be tapped off through a canal that passes from the exterior of the furnace to the bottom of the hearth, and which is usually kept closed with a plug of clay.

The top of the furnace connects with a series of fume chambers, which in their turn lead into a chimney. These chambers are not sufficiently extensive to condense much of the vapour that passes into them, but are chiefly valuable for arresting the particles that may be carried from the furnace by the force of the draught.

Starting a furnace of this kind after it has been repaired, requires much care lest a sudden change of temperature injure the walls; but a small quantity of fuel is put in at first, and a slight blast given, which, as the masonry becomes heated, may be increased.

The furnaces of Silesia will continue to smelt well only for about eight days, when it is found necessary, on account of the injury done to the interior by the intense fire, to discontinue the operation and make repairs.

The charge fused in the Silesian furnace consists of—

Galena, in small fragments,	100	parts.
Cast iron	12	„
Slag from iron forge.	14	„

For each ton of this charge a ton of coal is given, the fuel being thrown against the front of the furnace, and the ore against the back.

In the course of fusion, the galena gives up its sulphur to the iron, by the reaction heretofore referred to, while the iron slag serves to carry off the sulphur both by means of its oxygen and its metal.

The principal products of this smelting are—*rich lead*, which is passed to the cupelling furnace, and treated for its silver.

Slag, which is either so poor that it may be thrown away, or when it contains 7 or 8 per cent. of lead, it may be fused again.

And a *matt* or regulus, consisting of the sulphide of iron and lead, with a little silver, which is subjected to subsequent roasting and fusion, in order to remove the metal.

Five men are necessary, on each shift, to take charge of this furnace, and 50 tons of ore are on an average put through in eight days.

II.—TREATMENT OF ROASTED ORES IN CUPOLA FURNACES.

This plan is principally in use where it is necessary to smelt argentiferous galena in which earthy and metallic impurities are very abundant. At some establishments the ores are roasted in reverberatory furnaces heated with coal or wood, that are either furnished with a single hearth, or are constructed with one hearth above the other.

At others, the preliminary roasting is performed in heaps in the open air.

When the reverberatory furnace is used, the operation is commenced by charging the hearth with pulverised ore, by means of a hopper, or by throwing it in at the lateral doors. The heat is raised slowly, and the charge stirred continually, so as to present a fresh surface to the oxidising influence of the flames. When the oxidation has proceeded far enough, the doors of the furnace are closed, and a strong fire placed

upon the grate. Fusion soon commences, the quartz that may be present acts upon the bases forming silicates of the oxide of lead, of lime, baryta, &c., and the mass, consisting of these silicates and the oxide, the sulphate, and the sulphide of lead, is drawn out upon the floor of the furnace, allowed to cool, and broken with a hammer into fragments suitable to be treated in a cupola furnace.

This system, more or less modified, is in use in France, Belgium, and in many parts of Germany.

When the ore contains a very large quantity of a foreign sulphide, the roasting is sometimes performed in heaps in the open air. A portion of the products of the celebrated mines of Rammelsberg, on the Hartz, and Fahlun, in Sweden, are treated in this way. At the metallurgic works connected with the former, a remarkable species of roasting is performed, during which some of the sulphur of the ore is obtained. The ore, consisting chiefly of an intimate mixture of the sulphides of lead, iron, zinc, and copper, is piled in heaps formed in the manner shown in fig. 50. First,

Heap of Ore ready for Roasting. Rammelsberg, Hartz.

a thick layer of pine wood *a a a* is put down for the foundation; then the ore *b b* in pieces decreasing in size toward the top. Above this comes a layer of ore, already burned, which, being in a powdered condition,

completely encloses the heap, and prevents the access of too much air. A pile, when complete, contains about 150 tons of ore, and when kindled it burns chiefly through the decomposition of the sulphides, through a period of from eighteen to twenty-four weeks. Upon the top of the pile, pot-like depressions are stamped in the porous covering, and into these, the sulphur being sublimed from below, collects, and from time to time is dipped out in a liquid state. A little more than a ton of sulphur is usually obtained from a pile such as has been described, and this is found to be about sufficient to pay the cost of roasting.

The metallic products of the operation are roasted in a second and third heap. When most of the sulphur has been driven off, the remaining mass of fragments and powder is found to contain 4 to 10 per cent. of lead, 2 oz. 10 dwt. of silver to the ton, and a pound of gold in 73,000 cwt.

This is fused in a furnace constructed in the manner shown in the accompanying vertical section. The charge is mixed upon the floor *g*, and thrown with fuel by the aperture *c* into the shaft *s*, and here smelted by means of a strong blast projected through the tuyère, *t*.

The charge consists of—

35 cwt. of roasted ore,

10 cwt. of highly silicious slags,

$\frac{1}{4}$ to $\frac{1}{2}$ cwt. of oxide of lead and fragments of old cupels.

The quantity of lead in this charge forms 8 or 9 per cent. of the whole weight.

From $3\frac{1}{2}$ to $4\frac{1}{2}$ cwt. of lead is obtained, containing about one-eighth of a per cent. of silver, which, being cupelled, produces a silver containing a small quantity

*See note from Nevada m. s.
2 cents in a pound of ore*

rapid operation, less labour, and the production of a purer lead, while the operation may be discontinued and resumed at any time, and the cost of the furnace is less. On the other hand, the loss of lead on the hearths is very considerable, and goes far to diminish the profits that might otherwise accrue from their employment.

There are two systems of reduction in hearths in use—

I. *Reduction in the Scotch hearth, or Ore furnace.*

II. *Reduction in the American hearth.*

The former consists in roasting the ore in a rapidly increasing temperature in a reverberatory furnace, until a mixture consisting essentially of the sulphide and the sulphate of lead, in the proportion of two atoms of the former to one of the latter, is produced. This mass is thrown upon the hearth, and brought to a state of semi-fusion, by which treatment sub-sulphide of lead is formed, which being allowed to cool, a portion of metallic lead is released from combination, while the remaining mass takes on a higher state of sulphurisation.

The treatment in the American hearth differs from that in the Scotch hearth in the circumstances that unroasted ore, a wood fire, and heated air are employed. The air, acting upon the hot ore above the tuyère, forms the sulphate of lead, as in the Carinthian process, which, being heated higher, in connection with sulphide of lead, produces the metal and sulphurous acid gas by mutual reaction.

The operation of smelting lead in these apparatuses would at first sight seem to have a close resemblance

to the system of reduction in which the cupola furnace is used, since the hearth may be compared to a cupola furnace with a very short shaft. But a glance at the reactions which have just been mentioned, will make it apparent that in reality there exists a much closer relationship between the process carried out in the hearth, and that which goes forward in the reverberatory furnace, and which has been spoken of as the process by *double decomposition*, or by *reactions*.

THE BACKWOODS HEARTH.

Before speaking more particularly of the apparatuses known as the American and Scotch hearths, it will be interesting to notice a plan of smelting which is suggestive of post-diluvian art, and yet which, under the pressure of circumstances, grew up in very modern times, and was largely employed in an extensive lead-producing region. The hunter and settler in Missouri, in the United States, early learned to procure the lead necessary for making their shot and bullets, by building a fire in the hollow of a fallen tree or in an old stump, and smelting the pieces of galena that they picked up on the surface. The desired metal collected in the ashes, and required only a simple re-smelting to be ready for casting. It was an easy transition from this rude plan to the construction of logs or of rough stones represented in fig. 52.

The metallurgist would class this contrivance as a hearth without artificial draught. The front wall was about 8 feet long and 6 feet high, the bottom in the interior 2 feet wide and 8 feet long, growing broader in steps toward the top, thus forming a species of boshes.

The inclination of the interior is toward the arch in front, which serves to admit the air, and is temporarily

The Backwoods Hearth.

closed with a wall, except a small tap-hole from which the metal flows. The construction of this hearth was no more primitive than was the plan by which it was operated. A layer of heavy logs was laid down in the bottom, then followed a stratum of billets of split wood, upon which the galena was thrown, and the whole covered with a layer of small wood. The fire was kindled in the front arch, and the process of reduction commenced. The reduced lead flowed down through the front aperture into the basin. The combustion lasted about twenty-four hours, and about 50 per cent. of the weight of the ore was obtained in metal. The large proportion that remained among the ashes was partly collected by a subsequent treatment in what was called the *ash furnace*. This primitive plan of smelting lead is now obsolete, and its place is supplied by the more economical blast and reverberatory furnaces.

REDUCTION OF ORES IN THE SCOTCH HEARTH.

This system is in use in the counties of Durham, Cumberland, and Northumberland. The furnace is constructed, as is shown in the accompanying cuts, of which fig. 53 is a vertical section, along A B, and fig. 54

a ground-plan. It consists of a short shaft, *a*, with a tuyère, *t*, through which a strong blast of air can be

thrown. The shaft or cavity is 12 in. by 24 in., and 26 inches in depth, and is lined with plates of cast iron.

In front of the cavity is the work-stone, *c*, which is inclined forward and furnished with a channel, *d*, that leads into the iron pot, *B*. Above the furnace is a hood

of masonry, not shown in the cut, which carries off the fumes produced in smelting, and thus protects the workmen from their deleterious effects.

The ore is first roasted in a reverberatory furnace until much of its sulphur is driven off, the sulphate formed, and the mass agglomerated by a strong heat at the termination of the operation, by which means the mechanical loss by the fine particles being carried up the chimney is avoided.

When the work in the Scotch furnace shall begin, the cavity *a* is filled with peat, the blast put on, and the mass ignited. A few shovelfuls of coal are thrown upon this, and then an addition is made of a portion of the partially reduced mineral, known as *browse*, from a preceding operation, consisting chiefly of an intimate mixture of slag and the sub-sulphide of lead. After the furnace is fully heated, this *browse* is drawn out, and the refuse, or grey slag, is separated, while the remainder is given back to the furnace. If at this time it shows a tendency to be pasty, a little quicklime is added, to prevent clotting. The roasted ore is now thrown into the furnace, and subjected to the action of the heat; after an interval of some twenty minutes, the charge is again drawn upon the *working-stone*, the slag separated, and the metallic lead allowed to flow into the basin, *B*. The *browse* is then thrown back into the furnace, new fuel and ore are added, and thus the process continues. In a shift of twelve hours, a furnace such as I have described will produce $2\frac{1}{2}$ tons of metallic lead. The lumps of grey slag, which form an important result of the operation, are found to contain an average of 10 per cent. of the lead originally contained in the ore. They are laid aside for treatment in a slag hearth.

REDUCTION OF ORES IN THE AMERICAN HEARTH.

This apparatus, known as the American hearth, is in

some instances formed of cast iron. It is so arranged that a hollow case surrounds the hearth *H*, fig. 56, which furnishes a passage for the air on its way to the tuyère. After the furnace is heated, the blast is thus brought to a high temperature. The air enters through the

tube *c*, and following the course indicated by the arrows, it is at length driven out into the cavity *h*, through the tuyère, *t*. The ore being treated at *h*, the reduced metal flows down the channel *b* into the basin *B*, fig. 55. The strength of the blast is regulated by the workman by means of the valve *v*.

The hearth is first carefully warmed by means of a fire of charcoal or wood, and then the reservoir or cavity *h* is filled with lead, that soon assumes a fluid condition. Upon this bath the charge swims while being treated. The workman places several pieces of wood before the blast, and then charges with raw galena; the heat soon spreads through the whole pile, the before-mentioned oxidising and reducing action takes place, and the resulting metal flows off into *B*. When one charge is finished, a second of a similar character is made, and thus the operation continues. The use of a more concentrated fuel is found to give a too intense heat, and to prevent the rapid reduction of the ore and a heat sufficiently high to fuse the galena should never be used, and it is essential that a large quantity of air should be furnished.

At Rossie, in New York, in twenty-four hours 75 cwt. of lead are produced, and the cost of working, per ton, is about seven shillings.

In Carinthia this method has been used with ore giving by assay 70 to 71 per cent. of lead, and from this 61 to 62 per cent. of pure lead were obtained. It has been shown by accounts kept at Bleiberg, that in a hearth of this kind the expenditure of fuel amounted to 3.34 cubic feet of wood per hundredweight of lead. The hearth used in Przibram, in Bohemia, was found to produce 72 cwt. of lead in twenty-four hours.

CHAPTER XI.

THE PRODUCTION OF LEAD AND RICH LEAD FROM OXIDISED ORES
AND PRODUCTS.

THE oxidised ores of lead, such as the carbonate and the sulphate, occur in such large quantities in several localities that they are made the object of special operations. They are occasionally treated at the same time for the lead and silver that they contain. When they are found—as is generally the case—in intimate connection with galena, they are reduced by the methods already described for the latter ore.

The reduction of the oxidised result of the process of cupellation is, however, performed at a large number of furnaces. In some cases the litharge and the other oxidised products are argentiferous, and the rich lead resulting from their reduction is treated for its silver. In other cases, the litharge being formed from a poorer lead, is reduced, and at once given as soft lead to commerce.

THE TREATMENT OF CARBONATE OF LEAD.

Two methods are in use for treating this ore when it occurs without the admixture of sulphurous compounds.

I. *In the reverberatory furnace*, of which the hearth has a slight inclination toward an interior basin placed at one of the sides, and arranged with a tap-hole

through which the fused metal may flow into an exterior basin.

The ore is brought to the smelting house in the form of a fine sand, and mixed intimately with a quantity of powdered charcoal, anthracite, or coke, and some fluxes to render the earthy gangue more fusible. This mixture is shovelled into the furnace and spread upon the hearth. The doors are then closed, the fire raised slowly, and the charge stirred repeatedly; the heat is kept as low as practicable to prevent loss by volatilisation, and the lead, gradually reduced by the action of the coal and the gases, falls into the interior basin, and is allowed to flow out from time to time. This product is poured into cast-iron moulds, and after cooling, is sent to the cupelling furnace.

When the lead ceases to flow into the basin, the spongy materials that lie upon the hearth are heated until they fuse together; they are then drawn out, and sent to be smelted in a cupola furnace.

II. In the treatment of carbonate of lead in a *cupola furnace*, the ore should be in small pieces, or if, during dressing, it has been brought to the condition of a powder, this must be made into balls by mixing it with a small amount of clay, and drying.

A cupola furnace of the usual construction, about 7 feet high, is employed. The wind is thrown in at a single tuyère, and the gases produced by the operation are led into a large apparatus for condensation. The charge is made up of ore, impure litharge, bottoms of cupels, and fluxes. The operations are carried on rapidly, 5 to 6 tons being put through per day. The fuel is thrown in on the front wall of the furnace, and the ores behind. The carbon reduces the free

oxides of lead, as well as those in combination, and it hence becomes necessary that the coal or coke should be in excess, that the reduction may be complete, and that the slags may be in long and intimate contact with these reagents before falling from the furnace.

The products of the fusion are *slags*, which are carefully sorted, and those containing enough lead to pay for the operation are sent back to fusion; *fumes* which collect in the apparatus for condensation. These are sometimes very important, since in some cases 40 to 45 per cent. of the lead is volatilised. The largest portion of this is caught, and after moulding it into little bricks or balls, it is passed to the cupola furnace again. The lead produced is either concentrated by the process of crystallisation, or cupelled at once for its silver.

TREATMENT OF THE OXIDISED PRODUCTS OF CUPELLATION.

The oxidised substances which result from the process of cupellation, as litharge and the impure products known as *abzugs* or *abstrichs* (see page 159), are reduced in cupola and reverberatory furnaces, and occasionally in hearths.

The reduction of litharge in cupola furnaces.

For this purpose the most usual form of furnace is quite low, and so arranged that the lead falls quickly, after reduction, into the hearth and below the range of the blast. The upper and lower Hartz, Freiberg, and Silesia may be mentioned as regions where this system is in use. In the last named country a furnace of the form shown in the accompanying plan and section is employed.

The tuyère *t* is 27 inches above the bottom of the crucible *c*, and the front wall *w* rises 39 inches above the hearth *h*. The charge is thrown in over the front wall at *a*, and fusing down, the products rise through the hearth at *E*, and flow off, or are tapped through the canal *f*, into the basin *g*. The furnace is first well heated, and then the charge thrown in, the coal against the front wall *w*, and the litharge against the back wall *P*. The relative amounts of the two substances used is so arranged, that the coal shall be in the smallest

Furnace for Reducing Litharge.

possible proportion to produce perfect reduction. About every two hours and a half the workman taps off the contents of the crucible, consisting of lead and slags, into the basin *g*. The slags, which are rich in lead, are refused in a cupola furnace. The lead is dipped out of the basin and moulded into pigs. From 100 parts of litharge, 89 parts of lead are obtained. Twelve tons of litharge may be reduced with an expenditure of $2\frac{2}{3}$ tons of coal.

Reduction of litharge in reverberatory furnaces.

At Holzappel, in Nassau, I met with a system of revivification or reduction, in which the operation was performed in a furnace similar to that in use in

Carinthia, and which has already been figured at p. 111. This furnace is provided with a hearth 13 feet long by 8 feet broad, the upper surface of which is covered with a layer of vitrified slag. Beside the door, represented in the figure referred to, a second opening is made in the side of the furnace, near the fire-place, through which the charge may be thrown, and partly stirred. Care is taken in preparing the litharge for this furnace, not to bring it to a powder, but to retain it in pieces that will lie loose upon the hearth. About 600 pounds is shovelled in once, and well covered with a layer of stone-coal powder. The fire is then allowed to act $1\frac{1}{2}$ hours, when the workman begins a thorough stirring, but the fire is still kept moderate that the charge shall remain unfused. The lead reduces and flows into the trough that occupies the front of the furnace, where it remains in a fluid condition covered with glowing coals, until it is desired to dip it off into moulds.

The remainder on the hearth, after the lead ceases to flow, is brought to a state of semi-fusion, drawn out, and sent for treatment to a cupola furnace. About 40 cwt. of litharge is reduced in twelve hours, and the average quantity of lead obtained is 82 per cent. of the weight of litharge employed. Bundles of dry brush-wood are used as fuel. The cost of reducing each cwt. of lead in 1859-60 was about 5*d*.

The English and French establishments frequently employ a reverberatory furnace with a basin at the side, and the hearth inclined toward this basin. The fuel employed is usually stone-coal.

In some establishments the *Scotch hearth*, or an apparatus of a similar character, is in use for reducing the oxidised products.

CHAPTER XII.

THE TREATMENT OF RICH LEAD—SEPARATION OF LEAD AND SILVER—
CALCINING: PATTINSON'S PROCESS—GERMAN METHOD OF CUPELLING
—ENGLISH METHOD OF CUPELLING—EXTRACTION OF SILVER FROM
RICH LEAD BY MEANS OF ZINC.

THE various processes heretofore described, when applied to argentiferous lead ores, have concluded with the production of that important intermediary alloy of silver and lead known as *rich lead*. I will now proceed to detail the methods of separating the constituents of this compound, which methods are equally applicable to the products of the reverberatory furnace, the cupola furnace and hearth.

Before the era of modern improvements in metallurgy, the rich lead was passed directly to the cupelling furnace, there subjected to oxidation, and the two above-named metals thus obtained in a separate condition. But several extremely valuable processes are now, in many cases, made to precede cupellation, which have for their object the ultimate production of a more pure marketable product, the complete and more economical separation of the two metals, and the prevention of loss by volatilisation.

For an impure lead, such as is often produced on the continent, and containing a little zinc, copper, antimony, iron, or sulphur, a process known as *calcination*, is frequently in use.

With the object of producing a *marketable lead*

containing less silver, and a *rich lead* with a large amount of the more valuable metal, and at the same time securing the extraction of many of the above-mentioned impurities, *Pattinson's process* is in use. One or both of these operations are omitted in many furnaces, and the lead given, as formerly, directly to the cupellation.

CALCINING IMPURE LEAD.

The furnace used for this purpose belongs to the class of reverberatories, and is frequently constructed

Calcining Furnace.

as is shown in the accompanying cuts, Figs. 59 and 60, of which the former represents a vertical section, and

the latter, a plan. The sole, A B, consists of a cast-iron pan 10 feet in length by 5 ft. in width, 9 inches deep at the extremity, A, and 8 in. at the other end. This is placed in a horizontal position in the furnace upon a bed of sand, that it may have a perfect bearing for its inferior surface. The arch, c, is then sprung over this pan, rising but a short distance above it. The fire-place, D, is 5 ft. by $1\frac{1}{2}$ ft., and is separated from the lead pan by the fire-bridge, E, which rises 8 in. above the edge of the pan. The pot, H, serves, when required, to fuse the lead before introducing it into the pan, A B. The furnace is charged by carrying in the impure lead in the form of ingots, by means of a shovel, or by lading it into the pan after it has been brought to a fluid condition. The amount treated at once varies from 6 to 10 tons, it always being to the advantage of the manufacturer to have a large furnace; since more metal can then be treated with one heating. When now a strong fire is made in the fire-place, D, the easily oxidised impurities in the lead are acted on by the heated air and gases, float upon the surface, and may be scraped off by the workman. The appearance of the scum thus produced indicates the progress of the operation. When lead appears to be almost the only metal oxidised, the tap-hole of the pan is opened, and the contents run into an exterior basin, from which it can readily be laded into moulds. The length of time necessary for purifying lead by this means varies according to the amount of the adulterations present. For some impure varieties, thirty hours are required, and for 100 of the metal used from 70 to 75 pounds of lead ore obtained.

In Saxony a small reverberatory furnace is employed

in this preliminary process of purification. Two tuyères pass through the sides of this furnace, and a weak blast of air is forced through these upon the surface of the metallic bath, thus accomplishing the oxidation that is produced in the above described case, by the air entering at the fire-place.

PATTINSON'S PROCESS OF CONCENTRATING SILVER IN LEAD.

This process, for which the world is indebted to Mr. Hugh Lee Pattinson, of Newcastle-upon-Tyne, is the most valuable improvement in the metallurgy of lead and silver that has been introduced within the present century. It was invented in 1829, and in a very few years infused a new life into the lead and silver interest of the country. By decreasing the cost of separating the two metals, this process has made it possible to obtain an annual quantity of 200,000 ounces of silver, which was formerly thrown away. The process, even in 1836, was brought to such perfection that it was found by its use the cost of separating silver and lead was decreased to one-third the sum required to treat the argentiferous lead by the old method, and that lead containing but $\frac{8}{100000}$, or about 3 oz. to the ton, could be subjected to it with profit, while experiment showed that much commercial lead held at that period five times this amount of silver.

The principle taken advantage of by Pattinson may be exemplified as follows: When a large quantity—not less than two or three tons—of rich lead is fused in a kettle and allowed to cool gradually and equally, a vast number of small crystals form in the mass. These

crystals will consist of pure lead, while the fluid which surrounds them will contain the silver. If now these crystals be lifted from the kettle by means of a ladle furnished like a strainer with numerous holes, the argentiferous fluid will fall through, and the poor lead may be placed in a neighbouring vessel. The separation, however, cannot be performed at a single fusion. The crystals, although themselves probably free from silver in chemical combination, detain mechanically some of the argentiferous fluid, so that the separation is only partial, and two portions of lead will be obtained, one of which has more and the other less silver than the original rich lead.

If the poorer of these portions be again fused and allowed to cool, a second straining may take place, and a rich and a poor lead obtained, the latter of which, if treated in the same manner several times, will give in the end a portion of commercial lead almost entirely free from silver. The rich portion remaining in the kettles produces, after repeated fusings and strainings, a lead highly charged with silver, which may be sent to the cupelling furnace. The process is attended with the oxidation of many impurities, which are skimmed from the surface of the kettles, and thus the quality of the lead produced is usually excellent. A middling article, containing too little silver to pay for cupelling, may by this means be made to yield on one hand an excellent lead for the market, and on the other a quantity of rich lead that may be very profitably cupelled for its silver.

There are some differences in the plans adopted in the concentration of lead in various establishments, which are the result of the difference in the amount and nature of the rich lead to be treated. The most

important of these differences is in the quantity of crystals dipped out of the kettle at once.

In cases where the lead is poor, what is known as the *low system* is sometimes adopted, by which as much as seven-eighths of the contents of the kettle is dipped out at each fusion, as crystallised lead, and but one-eighth is allowed to remain. This system requires but few kettles, and the poor lead is quickly ready for market, but it can only with profit be applied to the varieties of lead holding little silver.

The plan in most general use is known as the *high system*, in which as little as two-thirds of the lead is strained out as crystallised lead, and the remaining one-third allowed to stay in the kettle. This system is best adapted for establishments producing much metal, and should be applied to all leads holding more than 9 to 10 ounces of silver to the ton.

APPARATUS FOR CARRYING OUT PATTINSON'S PROCESS.

The kettles in which the rich lead is fused are of cast-iron, built in and supported by massive masonry, as is indicated in the accompanying cuts. Figs. 61,

62, and 63 are intended to illustrate the position of a single kettle and the furnace adjoined. Fig. 61 is a

vertical section along the line E F, fig. 62 a vertical section along the line C D, and fig. 63 a horizontal section

along the line A B. The fire, built in the grate, *g*, plays around the under-side of the kettle, *K*, and the products of combustion pass off to the chimney through the flue, *f*. The size of the kettle employed varies with different localities. It should never be so small as to hold less than $2\frac{1}{2}$ tons, and in some furnaces, as in the Hartz, kettles holding 10 and 11 tons are employed. Of these kettles 9 or 11 are used in a single establishment, and they are placed in a long building in a row, as indicated in fig. 64.

MANIPULATIONS IN PATTINSON'S PROCESS.

If lead having 10 ounces of silver to the ton is to be treated, the kettle, *P*, is selected for commencing the operation, and say 140 cwt. are placed in it,

Arrangement of Kettles in Pattinson's Process.

and heated rapidly until fused. The heat is continued until the metal is raised to a temperature somewhat higher than that necessary to give it complete fluidity. The fire is then put out, and the mass in the pot partly cooled by throwing water upon it.

This must, however, be done with the utmost caution, since the water may become so surrounded by fused lead, that the sudden formation of steam will lead to explosions, dangerous to the men employed, and leading to a loss of metal. If a little more time is allowed, the cooling will take place without the necessity for the employment of water.

The mass begins to cool at the surface and along the sides of the kettle, and the crusts thus formed are carefully detached by means of a bar, and thrown back into the fluid, the cooling being thus caused to go on regularly. The stirring is at the same time continued regularly, that the crystals may form as free as possible from silver.

The ladle represented in figs. 65 and 66 is employed for lifting out the crystals. The lower part is formed of iron, and the upper of wood, that it may be more conveniently handled. It is kept warm, and before being used is plunged several times into the fused metal, that it may assume entirely the same temperature.

Fig 65

Fig 66

When the crystals have formed in a sufficiently large quantity, a ladleful is raised above the surface, and allowed to drain a few moments, and then, by a skilful movement of the workman, thrown into the neighbouring kettle, p' . The ladle is then re-warmed, and cleaned of the lead hanging to it, and the process repeated until about 80 cwt. are thrown into the kettle, p' . This portion is found to contain about 5 oz. of silver to the ton, or 50 per cent. less than the original lead. An additional 20 cwt. is now ladled out, containing about 10 oz. to the ton, and thrown into r . The 40 cwt. now remaining in p contain 20 oz. to the ton, and this is transported by means of a ladle without perforations to the kettle, r' .

The kettle, p , is now ready to be filled again, and the same course pursued. When the kettle, p' , is filled with lead holding 5 oz., it is allowed to cool and crystallise in its turn, and 80 cwt. of crystals are ladled from it, with $2\frac{1}{2}$ oz. of silver, and thrown into p'' , 20 cwt. with 5 oz. are laid aside to be returned to p' , and the remaining 40 cwt. with 10 oz. are transported to p or r . p'' is treated in the same way when full; 80 cwt. with $1\frac{1}{4}$ oz. are thrown into the kettle, p''' , 20 cwt. with $2\frac{1}{2}$ oz. are laid aside and given back to p'' , and the remaining 40 cwt. with 5 oz. are passed to p' . The lead in p''' with $1\frac{1}{4}$ oz. to the ton, is either considered sufficiently free from silver to enter commerce, and is simply fused and moulded for market, or it is made still poorer in silver, even to 12 dwt. per ton, but in many furnaces it will not pay to descend to this limit.

At the opposite end of the row of pots, the rich lead is at the same time being treated. When r' has been filled with lead holding 20 oz. it is fused and then

allowed to crystallise; 80 cwt. are ladled from it into R, with 10 oz. of silver to the ton, 20 cwt. with 20 oz. are laid aside to be treated again in R', and 40 cwt. go into R'', carrying with it silver to the amount of 40 oz. to the ton. When R'' is full, it is subjected to the same treatment, and R''' receives 40 cwt. with 80 oz. to the ton. The contents of R''' are crystallised, and produce for R'''' lead with 160 oz. to the ton, which in its turn is treated in the same way, and finally, 40 cwt. with 320 oz. to the ton is obtained in R'''''. In some furnaces concentration is carried still higher, and lead with 640 oz. is obtained. This is ready for the cupelling furnace, and is moulded into blocks and transported to that apparatus.

There are certain circumstances where the process of Pattinson is not applicable with profit. Thus, when the litharge produced by cupellation may be readily sold, and at a price higher than the corresponding quantity of lead. But when those products are difficult to sell, the method of concentration becomes advantageous. As a general rule, Pattinson's process is found employed for poor leads, but this is not because a lead having a comparatively large amount of silver could not be concentrated advantageously. But generally, where a very rich lead is produced, there is not enough of it to keep an establishment in regular operation, and it is usually seen to be cheaper to sell the litharge or reduce it than to go to the expense of erecting an apparatus for concentration.

The two grand products of concentration are a *soft lead for the market*, and a *very rich lead for cupellation*. A third product is the mass collected by skimming off the scum that rises to the surface of the kettles, and in which a large quantity of the impurities in the original lead are found. The loss of lead by the operation is

very small indeed, and does not generally reach $1\frac{1}{2}$ per cent. The silver is all to be found in the principal products, but that which remains in the soft lead may be considered as lost.

In cases where lead is very impure, where sulphur, antimony, arsenic, copper, iron, &c., are present, it is the custom in some furnaces to employ a simple means of purification, which may replace the plan above described, of *calcination* in a reverberatory furnace, when the amount of the impurities present is not too great. Such treatment is very necessary, since in impure lead the crystals do not form readily, and when formed they cannot be so perfectly drained from the fluid mixture of lead and silver as when but two metals are present. This plan of purification is known as *poling*. A large stick of green wood is moved through the molten lead; the gases given off by the wood set the contents of the pot in motion, and thus continually bring new portions of the metal to the surface and into contact with the air. The copper, iron, antimony, sulphur, &c., are thus oxidised, and, collecting upon the top of the metal, form a powdery crust that may readily be scraped off. Not only is this purification necessary for the proper success of the crystallisation, but it leads to the production of an excellent soft lead for market.

REFINING OR CUPELLING RICH LEAD.

As has been shown in the historical sketch at the commencement of this volume, the process of cupellation is distinctly mentioned in the Old Testament. The object of the operation then was, as it is at present, the extraction of the silver from the argentiferous lead.

We have seen in the chapter on the assaying of silver ores, that when lead is fused, and subjected to a current of air, it rapidly forms an oxide, which being lighter than the metal, swims upon its surface, and floats to the edges of the metallic bath, or may be removed. This oxide or litharge, when fused, is capable of dissolving the refractory oxides of several other metals, thus rendering them fluid, and easily conveyed away. When, however, silver is present, this metal does not partake of this oxidation, and consequently it remains behind, after the process, purified of nearly all the ignoble metals with which it was mixed. Upon this behaviour of the various metals are based all varieties of cupellation. There are in common use two distinct methods of cupellation, which we may study as *the German system* and *the English system*. In the former case, the hearth is formed of marl or other similar material; it is fixed, and of large dimensions, and the lead is often added all at once; in the latter, the hearth is movable, and is carried upon an iron car; it is made of bone ash, and its dimensions are relatively small, the formation of the litharge is very rapid, and the lead, instead of being given all at once, is added progressively, as the contents of the hearth are oxidised.

THE GERMAN METHOD OF REFINING OR CUPELLING.

This system may be found in use in most of the furnaces of northern and central Europe—in some cases rudely carried out, in others performed with much care and skill. The furnaces have sometimes solid, immovable arches of brick or stone above the hearth, but more frequently they are provided with a movable lid of iron coated with clay upon the interior, which

can be lifted off by means of proper machinery. I saw a fine furnace at Braubach, on the Rhine, where an arch of hollow bricks took the place of plates of iron covered with clay.

The above axinometric drawing will show clearly the form and construction of the German furnace. The

corner nearest the spectator is supposed to be cut away, that the interior of the apparatus may be better seen. The furnace, which is of the reverberatory class, consists of a circular portion containing the hearth, and a rectangular part containing the fire-place. The foundations, *FF*, are firmly built of stone, pierced with canals to carry off the moisture, and well cramped with flat wrought-iron rods, that pass across the body of the structure in various directions, and connect with the numerous vertical rods that are seen around the exterior. The fire-place, *A*, is arranged with a grate for burning either wood or coal, according to the locality of the establishment. The former fuel is the best for cupelling, since it gives a clearer and more oxidising flame, which can be regulated with more facility than that produced by the coal. The hearth, *H*, upon which the metal is fused and oxidised, is circular, like the body of the furnace, and is hollowed regularly, like a large saucer, from the edges towards the middle. It is composed of marl, or an intimate mixture of lime and clay, and is beaten by proper tools into the desired shape, while still in a moist condition. The hearth, *H*, is surrounded by a wall, *kk*, which serves to support the movable cap, *c*, which is formed of plate-iron well riveted together, strengthened by bars upon its upper side, and lined with clay that is secured in its place by numerous little iron straps. This clay serves to protect the iron from the influence of the flames, and requires to be frequently renewed. The entire cap is hung upon chains, and attached to the crane, *R*, by means of the lever, *L*. By this contrivance the cap, *c*, can be raised from its bearings and swung aside, when it is desired that the furnace shall cool rapidly, or when the hearth, *H*, is to

be repaired or renewed. The aperture, κ , in the wall, κ , opposite the fire-bridge, $\mathcal{B}$, serves to introduce the mass from which the hearth is made, and the lead to be treated, and also as a sort of chimney, through which the products of combustion pass from the hearth. A second aperture in the corner, that is represented in the figure as being cut away, serves to draw off the oxidised products, and for the workman to watch the course of the operation. Opposite this aperture, at τ , are two iron tuyères, that are so inclined that a strong blast may be thrown through them towards the middle of the hearth, but are so arranged that the workman may give the wind any direction that may appear desirable.

The dimensions of these furnaces vary in different localities. At Clausthal they are 10 ft. in diameter, and from 8 to 10 tons of lead are treated at once. At Altenau, the concentrated lead from Pattinson's process is treated in furnaces 8 ft. in diameter, and receiving five tons at once. At Clausthal, where wood is used as fuel, the fire-place is 6' 6" long and 1' 6" broad; and the cap, c , is 9 ft. 9½ in. in diameter.

The pressure of the wind thrown through the tuyères at τ , should be strong enough to form little waves on the surface of the fused litharge, and drive them towards the opposite working door.

CUPELLATION IN THE GERMAN FURNACE.

Each operation in the German cupelling furnace must commence with the formation of a hearth. This is composed, as before stated, of marl, or when marl cannot be obtained, of a compound of lime and clay,

prepared by powdering the two constituents, and mixing them intimately. The proportion of clay in this case should be only large enough to make the mass tenacious.

Marls, when homogeneous, are preferable to any artificial compound of lime and clay, since it is difficult to obtain by mechanical means a mixture of these substances so perfect as that formed by nature. The marl is prepared by stamping it finely in a mill belonging to the furnace, and after passing it through a sieve, mixing it with the remains of old hearths—also stamped and sifted. The workman considers the material best adapted for his use when he has moistened it sufficiently to make it mould well when squeezed in the hand, but at the same time not wetting the skin.

This mass is now brought to the furnace, and either stamped layer after layer in the hollow prepared for it, or it is all put down at once, and in one layer, and by beating it with a proper instrument of wood it is brought to the form shown at H. The operation is terminated by giving the surface an extra firmness and smoothness by means of stampers of cast iron.

In some furnaces leached ashes, with a small admixture of lime, are employed. This was the ancient material for hearths, but it is found to absorb too much lead and silver, and to be more variable in its character than artificial or natural compounds of clay and lime.

The hearth being ready, the rich lead is charged by laying down a thin bed of straw, and piling the pigs carefully upon it in such order that they take up the least space. The cap, c, is then placed by means of the

crane, in its proper place, luted around the edges with clay, and the fire started in the grate, A.

In most cases the rich lead contains, beside silver and lead, several per cent. of other metals, the greater portion of which is oxidised in the early part of the process. Soon after the metal is fused, its surface is found covered with a dark crust, which consists of the oxides of these metals, and also of earthy substances that formed impurities in or on the rich lead. This crust is drawn off through the working door opposite T by means of a piece of wood attached to the end of a long bar of iron. The fire is kept strong enough to maintain the lead at a dark red colour. The impurities are gradually separated, and at the end of several hours—depending in number upon the amount of impurity present—the oxide of lead is found to be almost the only product that comes from the furnace, and this flows out readily, since it is very fluid when fused in an unmixed condition. The first dark materials drawn from the furnace are known as *Abzugs*; those a little more fluid, that come after, are called *Abstrichs*; and, still later, the *cupreous* or *wild litharge* forms, and flows from the furnace.

Now commences the formation of the litharge proper, with the aid of the blast. The temperature is kept almost stationary until the end of the operation, between a cherry and a bright red, at which degree the litharge takes a high degree of fluidity. The air is driven in at the above-mentioned nozzles, with the pressure of about an inch of mercury. The wind is so regulated that it produces the proper sized waves of litharge, strikes the fluid metal upon a large part of its surface, and at the same time does not disturb the

draught of the furnace. It requires long practice to enable the workman to arrange the heat and blast to the best advantage, and to draw out the litharge in the proper manner.

The litharge obtained from the furnace during this second period is the most pure produced. Two varieties are distinguished, the *yellow* and the *red*. The first has a yellowish shade, and is fused together in grains or pieces. The second exists in a finely divided condition, as small scales or flakes. These varieties arise simply from their mechanical condition, which is the result of different circumstances in cooling. In trade, the red variety is far the more sought, and hence the furnace-man often endeavours to produce more of this sort by running the products of the furnace into large vessels of iron, and allowing it to harden in large masses, since it is only necessary that the cooling shall take place very slowly to produce the desired flaky condition. In some instances the vessels are heated, in which case a still larger quantity of red litharge is obtained.

Subjected to a continual heat and oxidation, the lead in the furnace gradually diminishes in quantity, until at length the contents of the hearth consist of silver with but 2 to 3 per cent. of lead. Then the appearance which is mentioned in the chapter on assaying, page 81, is observed, the contents of the furnace assume a more brilliant surface, and the brightening is said to take place. This indicates that the period for the conclusion of the operation has arrived. Water is thrown in, the silver hardens to a cake, and is drawn from the furnace by means of iron bars, cleaned of the marl and litharge, and transported to the magazine to await the second process of refining.

The time necessary for accomplishing this cupellation will vary with the treatment and the amount of lead taken at once. In the case where the charge amounts to 10 tons upon a hearth 10 feet in diameter, sixty-six to seventy hours will be required.

In some furnaces the lead is not all put in the hearth at once, as above described; but after the first charge has partially oxidised, more fresh lead is added, and oxidation and addition are repeated several times. This system produces an impure litharge, but a larger quantity of lead can be treated at once. Upon the process being finished, and the silver removed, the movable cap, c, is taken off, the furnace allowed to cool, and a greater part of the hearth broken out and fused in a cupola or reverberatory furnace with the proper admixture of fluxes, in order to recover the silver and lead that have penetrated it.

The early products of oxidation, containing many impurities, as iron, zinc, antimony, sulphur, arsenic, &c., with much lead and some silver, are given back to the fusion for rich lead, or reduced separately, forming an impure alloy, usually containing much antimony, which serves for making shot or preparing the alloy used for making type. At the last part of the operation, just before the *brightening*, the litharge is very rich in silver, and is hence carefully laid aside, reduced separately, and cupelled for the precious metal.

THE ENGLISH METHOD OF REFINING OR CUPELLING.

The chief differences between the German and the English plan of cupelling have been mentioned at page 154. Pattinson's process of concentration is now

usually made to precede this method of cupelling, and hence a very rich lead is generally subjected to oxidation, but previous to the introduction of the improvements of Mr. Pattinson the plan was in use for leads with but little silver. Lead containing from 9 to 11 ounces to the ton, however, did not admit of being cupelled with profit. Since so much metal had to be oxidised, a very large quantity of fuel was required, and at least 7 per cent. of the lead brought into the furnace was lost. The introduction of *concentration* made it possible to subject but a small quantity of lead to oxidation in order to secure the silver, and hence but a comparatively small loss of lead and expenditure of fuel was incurred.

The furnace employed is much smaller than that last described, and in its construction it presents many peculiarities.

In the accompanying cuts of this apparatus, fig. 68

represents a vertical section along the line *c d*, and fig. 69 a horizontal section along the line *A B*. The furnace is of the class of reverberatories, with a fire-place, *a*, a fixed vault, *B*, and a chimney of small elevation, *p*. The bone-ash hearth, *H*,

is placed upon the iron car, *c*, which runs on rails, and may readily be

drawn from beneath the vault when desired. The wind is thrown in through a nozzle at *w*. The construction of the cupel or hearth may be understood by a reference to fig. 70, which gives a plan, and fig. 71

a section along the line *E F*. The hearth is about 5 feet long, 40 inches broad, and 5 to 6 inches deep. Its circumference consists of a strong wrought-iron ring, nearly elliptic in shape, and with a framework of iron bars across the bottom, as shown by the dotted lines in fig. 71. This iron periphery is known as the *test ring*. In order to prepare the cupel, this frame is beaten full of finely-powdered bone-ash that has been moistened with water in which a small quantity of the carbonate of potash has been dissolved. The hollow shown at *b* is carefully and regularly shaped with a trowel, until the bottom remains about one inch thick above the iron bars, *t t t t*. The opening, *L*, fig. 69, serves to introduce into the hearth the rich lead which has previously been fused in a kettle near the furnace, and the door, *o*, allows the litharge to flow from the hearth into the pots placed in front to receive it. The fire-place, *a*, is 15 inches by 4 feet, the fire-bridge, *b*, 30 inches long, the chimney, *p*, 10 inches square. The blast thrown in through the tuyère at *w*, is arranged to introduce from 18 to 20 lbs. of air per minute.

MANIPULATION IN CUPELLING RICH LEAD BY THE
ENGLISH METHOD.

The cupel, after having been formed as above described, is dried for several days, and then introduced beneath the arch, *B*, and wedged firmly in its place. The coal fire is lighted in the fire-place, *a*, and the furnace heated very carefully, lest the cupel should crack. When the temperature reaches a dark red, lead which is kept fused in a kettle near by, is poured into the cupel, *H*, by means of a long-handled ladle, the blast is put on, and the fire raised until the lead reaches a bright red heat.

The formation of the litharge takes place rapidly, and as fast as produced it is allowed to run off through a channel in the cupel, which is kept at a constant depth. As the lead is oxidised, and its level grows lower, more molten rich lead is poured in through the aperture *L*, and thus about 500 or 600 lbs. of metal are constantly kept in the hearth. The litharge is received in large cast-iron pots, allowed to cool, and taken from the vessels in a solid state, by turning them upside down. Since the silver remains in the hearth, while the lead oxidises and flows off continually, the proportion of the former metal constantly increases. When 4 or 5 tons have been added, and the mass in the hearth has been concentrated until it contains about 8 per cent. of silver, the operation of the furnace is arrested, and its contents run out into moulds. A second shift is then commenced by giving 500 or 600 lbs. of fresh lead to the cupel, and proceeding as before. Thus a single cupel will often last forty-eight hours, and 6 or 7 tons of lead may be oxidised upon it.

SECOND OPERATION IN ENGLISH CUPELLING.

The lead in which the silver is concentrated until it exists to the amount of 8 per cent. is run off into moulds and laid aside for an especial treatment. The cupel, formed as above described, is placed in the furnace and brought to almost a bright red heat; about 600 lbs. of lead are then added, after having been fused in a neighbouring kettle, and a strong current of air given. The lead immediately begins to oxidise, and the litharge produced flows off into a vessel provided for the purpose, while at the same time the attendant adds lead to keep the level of the metal in the cupel always at the same point. Thus some three tons of the alloy of lead and silver are given, and about 500 lbs. of silver are collected in the cupel. The attendant then ceases to add rich lead, and allows the silver to purify. The before-mentioned phenomenon of brightening is soon perceived, the fire is lowered, the wind stopped, and the cake of silver allowed to cool slowly. The iron car with its subjacent hearth is now drawn from beneath the vault of the furnace, the silver taken from its bed in the bone-ash, cleaned of its coating of impurities, and given over to the process of refining. It is either purified by melting in a plumbago crucible, or by a second oxidising fusion in a bone-ash cupel.

The litharge produced in this last operation gradually grows richer in silver to the end of the cupellation. It is all reduced to a lead containing usually from 30 to 40 ounces of silver to the ton, and, after being treated by concentration, is again given over to the cupelling furnace.

THE EXTRACTION OF SILVER FROM RICH LEAD BY
MEANS OF ZINC.

When argentiferous lead is fused with zinc, the metals well stirred together and afterwards allowed to remain quiet for some time, the zinc will rise to the surface, and will be found to contain nearly all the silver. If the argentiferous zinc be now skimmed off, or allowed to grow solid and form a crust that may be raised and separated from the lead, and then treated for its silver, the latter metal may be obtained in an unmixed condition.

This superior attraction of silver for zinc was applied by Parkes to the extraction of silver from rich lead, and the plan that he contrived is known as "Parkes's process of de-silverising lead."

This process was introduced at the Works of Messrs. Nevill, at Llanelly, with good success, and was carried out as follows:—

In an iron kettle resembling those that have been described as in use in concentration by crystallisation, about 6 tons of lead containing about 14 oz. of silver per ton are fused. Into this about 1 per cent. of fused zinc was poured, and four men stirred the fluid metals for from one to two hours. The fire was then lowered, and the mixture allowed to rest for some time until a scum formed, which was removed with a ladle in which a number of holes were pierced. When the crust ceased forming, the lead was run off into a reverberatory furnace, and heated in a flat pan, to allow the zinc that may have remained in it an opportunity of evaporating or oxidising. When sufficiently treated here, it was run

into an iron pot, stirred with a stick of green wood to bring about a still more perfect oxidation, and then moulded for sale.

The scum taken from the pot was partly purified of the lead with which it was mixed by heating it in a sloping iron retort. The lead that ran out of this zinc contained about 1000 oz. of silver to the ton, and was ready for cupellation. The remainder in the retort was treated in clay pots, and the zinc distilled out. A residue was obtained, consisting of silver mixed with much antimony, lead, copper, arsenic, nickel, &c., which mixture was fused with lead and cupelled for its silver.

The loss of lead in Parkes's process was said to be about 1 per cent. On account of the difficulty of treating the compound of silver and zinc, this plan has been relinquished during the last two years. Experiments made in Hungary are said to have resulted favourably for this method.

CHAPTER XIII.

EXTRACTION OF SILVER FROM ORES AND PRODUCTS BY AMALGAMATION:
THE EUROPEAN SYSTEM—THE AMERICAN SYSTEM—THE SYSTEM OF
AMALGAMATION IN KETTLES.

THE metallurgic treatment of the ores and products containing silver that have hitherto claimed our attention, have been dependent for their efficacy upon the disposition of silver under certain circumstances to form an alloy with lead, to the exclusion, more or less perfect, of most other elements.

By this means an argentiferous lead was obtained, and the two metals were separated by a process founded upon the fact that lead has a far greater attraction for oxygen than silver.

Quicksilver resembles lead in possessing a greater attraction for silver than for most other elements. If the two metals are brought together, even at common temperatures—the quicksilver, like the lead in the foregoing instance, being in a fluid condition—a *rich quicksilver*, or an amalgam will be formed, in which both metals will retain a reguline condition. This important compound of mercury and silver may have the latter metal in various proportions, but when it reaches 35 per cent. the mercury will be saturated.

If it is desired that this intermediary compound or amalgam should now be treated for the separation of the two metals, the unique property possessed by mercury of taking on the form of a vapour at a low temperature is brought into play. The quicksilver is evaporated from the amalgam by heating it in proper vessels, and the silver obtained in a metallic condition as a residue.

This, in a very few words, is the plan of obtaining silver by amalgamation, which is now largely employed in working ores in various parts of the world. Numerous varieties have been contrived to suit the circumstances of different localities, or have developed as knowledge increased, and numerous modifications are necessary in working various ores.

The ancient Romans used quicksilver to amalgamate and collect the gold that remained in old lace and similar ornaments, but we have no account of its being employed on a large scale for working ores. An Arabian manuscript speaks of the employment of quicksilver in

amalgamating gold sands by the negroes of Nubia, in the twelfth century, as though it were a fact well known. But little or no use however appears to have been made of mercury for extracting silver from its ores before the middle of the sixteenth century, when a process was discovered in Mexico by Bartolomé de Medina, and shortly after transported to Peru by Velasco. The introduction of the system into Europe was proposed in 1588, but the subject was soon dropped, and a period of 200 years passed without its being again broached.

In the meantime circumstances favoured experiment in South America, and a priest named Barba, a native of Andalusia, modified the early plan of amalgamating in heaps, and introduced the amalgamation in copper kettles. And in 1784 Born, an Austrian mining officer, imported into Europe the improved process of Barba.

The establishment of amalgamating works in Hungary created a remarkable sensation in the metallurgic world, and in 1786 engineers and mining officers from Cornwall, Norway, Prussia, Hanover, and Saxony, met in the remote town of Chemnitz, attracted by the fame of the novel process. From Hungary the system was transported to Freiberg, and, after being essentially modified by Gellert, was put largely in practice. Thus the Saxon or Freiberg method of amalgamation grew from the primitive plan of Medina, and only after two-and-a-half centuries arrived at the state of perfection in which it was introduced into the furnace on the Mulda. The system continued in use at this spot until some five years ago, when the process was relinquished, because of the large sum that was required for wages, the incompleteness with which some of

the ores could be worked, and because the experience of half a century had so improved the plan of reduction by fire, that it could be employed more economically than when the new process was introduced in 1790.

The system of amalgamation is especially suitable for localities where fuel is very dear, and where it is hence desirable to extract the silver from its ores with the aid of little or no artificial heat. Those ores that are eminently adapted to this treatment are such as contain but little silver, and are of an extremely refractory nature.

In describing the systems in use for amalgamating silver ores, three varieties may be distinguished—

- I. *The European system of amalgamation in casks.*
- II. *The American system of amalgamation in heaps.*
- III. *The system of amalgamation in kettles.*

I.—THE EUROPEAN SYSTEM OF AMALGAMATION IN CASKS.

The works near Freiberg in Saxony furnished the best model of the European system of amalgamation. At present establishments employing the same process are in operation in Hungary, and in various parts of Mexico.

At Freiberg the ores destined for amalgamation were chiefly of a pyritiferous nature, and held from $\frac{1}{16}$ to 2 per cent. of silver. They were brought to a finely divided condition and mixed together until an average of about $\frac{1}{3}$ d per cent. of the precious metal was obtained in the mass, and were then intimately mixed with from 10 to 14 per cent. of common salt, and given over to roasting.

This operation was performed in what is known as

the Hungarian reverberatory furnaces in charges of $4\frac{1}{2}$ per cwt. The treatment here required the utmost care; first, by a gradually increasing temperature to oxidise the sulphides, and then by a stronger fire to produce a reaction between the sulphates thus formed and the chloride of sodium, and the consequent production of the chlorides of the various metals. By this means the silver was almost entirely transformed into a chloride.

The roasted ore, which had assumed the appearance of a brown powder, was then passed through a sieve, and the product brought to the building containing the machinery for amalgamation.

The argentiferous mass was first introduced into a cask, arranged as is shown in the accompanying drawing, Fig. 72.

This vessel was well bound with iron, and fixed upon the axis *a*, so that it could be made to revolve by means of the cog-wheel *w*. The roasted powder to the amount of 1000 lbs. with 300 lbs. of water, and about 110 lbs. of wrought-iron, were introduced through the opening *b* into the cask, and the aperture then closed firmly with a screw.

The manner in which the charge was introduced and treated, will be made clear by a reference to the adjoining section of the machinery employed. The chest, *A*, in the second story of the building was provided with the proper quantity of ore. The cask, *c*, similar in construction to that shown in the figure, was placed

Cask used in the European Amalgamation.

in the position in which it is here seen, and by means of the hose, *e*, the powder falling through the pipe, *m*,

Disposition of the Machinery used in the European Amalgamation.

was conveyed directly into the cask. The box, *B*, held

the proper amount of water, which could readily be carried by a tube into *c*. The charging being finished, the bung *f* was screwed tightly in place, and by means of the driving-wheel, *d*, which was set in motion by water power, the cask was given fourteen to sixteen turns per minute for a period of two hours. During this time the soluble salts formed during roasting were taken up, and the whole mass brought to a broth-like consistency. The mercury was now added, being introduced by a tube from the trough, *q*, which connects with a reservoir, and then follows twenty hours' constant turning, at the rate of twenty-two times per minute. During this period the chlorine of the chloride of silver, combined with the iron, and the silver thus set free, were taken up by the quicksilver forming an amalgam, and this chemical activity produced at the same time considerable heat which aided in making the decomposition rapid and complete. At the same time some copper, lead, antimony, and gold, if they are present, are taken up by the mercury.

The cask was now two-thirds filled with water, and its motion decreased to eight or nine times per minute, for two hours. This treatment served to collect all the amalgam in a single mass, and prepare it for drawing off through the small hole with which the bung *b*, Fig. 71, was pierced. At the end of this period, the cask was turned with the bung downwards; a tube attached to the opening, and the amalgam allowed to run into the trough *h*, the remainder of the contents are then emptied into the trough *i*. This remainder, after the water was deducted, contained from $\frac{1}{60}$ th to $\frac{1}{120}$ th per cent. of silver. When it held above $\frac{1}{100}$ th per cent., it was dried, re-roasted, and again submitted to

the action of mercury. Immediately upon falling from the cask, it was transported by the trough *i* to a proper reservoir, where it was continually stirred by machinery, that the small grains of amalgam with which it was mixed might fall to the bottom and be collected.

The amalgam from the trough *h* was placed in close canvas bags. A considerable portion of the quicksilver containing about $\frac{1}{30}$ th per cent. of silver, filtered through the pores of these bags, either by its own weight or when subjected to a slight pressure. A mass was thus obtained that did not pass through the stuff, containing from 10 to 12 per cent. of silver, and 4 to 6 per cent. of copper. This mass was then brought into iron retorts, and by the application of a proper heat, the quicksilver was distilled over, and collected in a condenser. The portion remaining behind consisted of silver and various impurities, which, after being refined in an iron crucible, was sent to the mint. The quicksilver was collected from the condensing chamber, and given back to the amalgamating casks.

The loss of silver by this process of amalgamation was from 5 to 9 per cent. of the amount contained in the original mineral, and but $\frac{1}{20}$ th of a pound of quicksilver was lost for each cwt. of ore amalgamated, or between $\frac{1}{4}$ th and $\frac{1}{5}$ th of the weight of fine silver produced.

The amalgamation of the argentiferous sulphide of copper or regulus, which at one time took place at Mansfeld, the system of amalgamating the impure copper now in use in Hungary, and the treatment of the *speise*, or the argentiferous remains in the smalt manufacture, all resemble in their general plan the system above detailed; but on account of their limited importance they do not require special description here.

II.—THE AMERICAN SYSTEM OF AMALGAMATION IN HEAPS.

The American system of amalgamation differs from the European in requiring for its accomplishment but little machinery, in being more wasteful of quicksilver, and in necessitating a longer time for carrying out its various processes. It is also different in the nature of the chemical reactions upon which it rests, as will be observed in the following description. It is very largely in use in Mexico and Peru, and is particularly suited for those remote mountain districts, where fuel and motive power are difficult to obtain.

The silver exists in these countries in veins running through crystalline and Plutonic rocks, and in a native state, or combined with chlorine, bromine, iodine, sulphur, antimony, and arsenic. In the greater number of veins, the portions nearest the surface have been much changed by the influence of the atmosphere and the surface water. These parts usually contain the precious metal in an uncombined condition, or as a chloride or iodide distributed regularly in a gangue of quartz or oxide of iron. At a lower level the compounds of sulphur and arsenic are more generally found.

In the preparation of the minerals for metallurgic treatment it is sought to separate the compounds of antimony, sulphur, and arsenic, from those containing the silver in a native state, or combined with chlorine, bromine, or iodine. The former minerals constitute what are known as *negros*, and the latter are denominated *coloradoes*, and the metallurgic treatment to which the two should be subjected is quite different.

The average richness of the ores treated in Mexico is about 0.25 per cent.

See 1251 - Same

The *coloradoes* are usually well sorted by hand at the mouth of the mine, and in a few instances submitted to the usual concentration by washing. The sorted ore is then stamped by machinery put in motion by mules or water power, and then ground fine in peculiar native mills known as *arastras*, which consist of a circular bed of hard stone, smoothly dressed and surrounded by a wooden tub. In the centre a pivot sustains four arms, to which are attached the same number of *mullers* or heavy flat stones, by which the grinding is effected. These stones are made to move around upon the hard circular bed by the power of mules attached to the extension of two of the arms. The ore from the stamping mills is mixed with water, and treated in this apparatus until a very fine powder is produced.

The ground ore is now deposited in basins of mason-work, and allowed to remain until a greater part of the water is evaporated. It is then transported to the court of the *hacienda*, as the amalgamating establishment is generally called, and there thrown into a heap usually 10 inches high, and depending in size upon the amount of ore to be treated. When, for instance, 50 tons are to be worked, its diameter will be about 50 feet.

Upon the top of this bed of ore is thrown an even layer of common salt, amounting in quantity to about 2 per cent. of the ore. The salt is allowed to dissolve gradually, and in order to produce a homogeneous mixture, the heap is turned with the shovel, and horses and mules are driven around upon it for several hours. After this treatment it remains untouched for about a day, and then the attendants proceed to add the *magistral*.

This important agent in the American amalgamation

is made by roasting at a low temperature the sulphide of iron and copper. When of a good quality it should contain about 20 per cent. of the sulphates of these two metals.

From 1 to 2 per cent. of the *magistral* is mixed with the ore, in the same manner as the salt, and the heap well stirred by driving mules upon it; or, where the absence of food for animals makes their support too expensive, the workmen themselves walk round and round upon the soft mass.

When the mixture is complete, the first addition of mercury is made. The metal is added, to the amount of about four times the weight of silver shown by assays or estimated by the directors to be present in the mass. It is thrown evenly over the surface by squeezing it from a leather or canvas bag. After this addition a *repaso*, or tramping by mules, horses, or men, is accomplished, and then the heap is left undisturbed for some time, until the assays that are taken every day show that the operations should be hastened by the addition of fresh *magistral*, or made slower by throwing in lime, ashes, or other alkaline substances, and in either case following the addition by a thorough mixing by *repasos*. When the assays show that the mercury has been entirely taken up, a second addition of about three-eighths of the quantity originally employed is made, and the tramping and daily assaying continued. A third, and even a fourth, addition of mercury is often found necessary; and when at length the assays show that all the silver in the heap has gone over into the amalgam, this treatment is discontinued, and the mass given over to the *washing*.

SEPARATING THE AMALGAM FROM EARTHY IMPURITIES.

The entire heap, or *torta*, is now transported from the court where it has been treated, to neighbouring vats, into which it is thrown, together with as much fresh mercury as has already been given, and a large quantity of water. Here it is stirred continually by means of a vertical paddle-wheel moved by four mules, and the amalgam falling by its specific gravity to the bottom, is dissolved and retained by the fresh mercury, while most of the worthless material remaining mechanically suspended in the water is carried off. At the bottom of the vat will now be found collected, the silver dissolved in the mercury, and a certain amount of heavy, metalliferous matter, in which is contained some silver. The argentiferous mercury is separated from this mineral mass, and the latter, after concentration by washing, is given back to the amalgamation.

TREATMENT OF THE AMALGAM.

The liquid amalgam, after being removed from the vats, is put into strong canvas bags, through which the mercury percolates, leaving behind a pasty, argentiferous compound, consisting of about one-sixth of silver and five-sixths of mercury. This is moulded and compressed by proper apparatus into triangular forms, and is now ready to be given over to distillation.

The triangular bricks of amalgam are piled in a column upon an iron grate above a reservoir of water, which is intended for the condensation of the fumes of the metal. The pile of amalgam is then covered with an iron bell, the edges of which are luted down, and

the metal to be treated thus hermetically enclosed. Around the iron bell a wall of loose stones is constructed, and in the circular enclosure formed by this means, a strong charcoal fire is made and continued during eight, ten, and even twenty-four hours, according to the amount of amalgam treated and the size of the apparatus employed. The apparatus is then allowed to cool, and the mercury is found separated and condensed in the interior reservoir, while the silver, in a spongy form, and almost a pure condition, is removed and fused upon a hearth of bone-ash, moulded into ingots, and then sent to market.

The duration of this process of amalgamation depends upon a number of circumstances; as the nature of the minerals employed, the frequency of the *repasos*, and the purity of the re-agents. The temperature of the atmosphere in which it is carried on has also a great influence; the operation is conducted differently in the winter and in the summer, in the establishments situated in elevated regions and those near the level of the sea.

When the circumstances are most favourable, the time necessary is about twenty-five days, but often it requires from forty-five to sixty days. Since accurate assays are seldom made, it is difficult to arrive at the loss of silver in this operation, but it is generally conceded that only from $\frac{3}{4}$ ths to $\frac{4}{5}$ ths of the entire amount in the ore is obtained. The loss of mercury is also variable, and depends greatly upon the care and knowledge of the directors of the work. In the most favourable cases it amounts to $\frac{1}{4}$ th of the weight of silver obtained, while under some circumstances it reaches $1\frac{4}{5}$ ths.

The class of minerals which have been described as

negros are either amalgamated directly or subjected to a previous roasting. In the latter case the amalgamation is conducted nearly as has been described.

The direct treatment of this sort of ore is, however, attended with much more loss of silver than takes place in the case above described, the loss being from 35 to 40 per cent. of the silver present ; or in other words, it reaches from four to five times the loss incurred in the amalgamation in casks.

In this plan of amalgamation practised in America, the silver of the ores is converted into the chloride, as we have seen was the case in the European method, but it is here done by the wet way, instead of by the aid of artificial heat.

The chloride of sodium, which is disseminated through the heap in a finely divided state, acts upon the sulphates of iron and copper of the *magistral*, and the sesquichloride of iron and the chloride of copper are produced. These in their turn act upon the silver, which is present in a native condition as sulphate or as sulphide, and the chloride of silver is formed. The quicksilver now decomposes this compound of silver, producing a sub-chloride of mercury, or calomel, while on the other side metallic silver is set free, and is dissolved by the mercury, producing amalgam. The loss of quicksilver is here necessarily greater than in the case of the European amalgamation, where it will be remembered the chlorine is made to combine with iron instead of the much dearer quicksilver.

The following interesting extract from the books of the Real del Monte Company, one of the most important in Mexico, exhibits the relative expense of three systems of working the ores of silver, by barrel

amalgamation, by amalgamation in heaps, and by smelting. The average yield of the ore in 1849 was 78 dollars (dollar = 2s. 10d.) per 3000 lbs.

TABLE, SHOWING PRODUCE OF SILVER AND COST OF EXTRACTION AT THE ESTABLISHMENT OF REAL DEL MONTE COMPANY.

Sources of expense for 3000 lbs. of ore.	By barrel amalgam at Velasco.	By amalga- mation in heaps at Regla.	By smelting at Regla.
Stamping ; for labour	\$00·59	\$00·26	\$00·30
Wear of stamp heads	·25	·28	·23
Grinding ; mostly for labour	·70	·83	...
Drying and lifting ; mostly for labour	1·20	...	...
Calcination " "	1·76	...	...
Amalgamation in barrels and heaps ; mostly for labour }	1·04	3·98	...
Smelting in furnaces ; mostly for labour	...	...	17·80
Wear of barrels	·30	...	...
Distilling amalgam and casting silver	·10	·05	·04
Repair of machinery, furnaces, &c.	·60	·48	3·90
Sundry costs	·30	·40	3·40
Fuel, wood	3·31	...	1·00
Fuel, charcoal	·30	·20	34·90
Salt	5·37	3·64	...
Sulphate of copper	...	2·13	...
Litharge	...	...	21·50
Tallow and oil for machinery	·37	·10	...
Quicksilver	2·39	4·32	...
Steam power ; mostly for fuel	4·23	...	...
Animal power ; mostly for forage	...	...	...
Salaries, expenses of management	1·14	1·09	6·80
Total cost of reducing 3000 lbs. of ore.	23·95	17·76	89·92
Mean produce of silver per 3000 lbs. of ore.	94·80	65·92	514·40
Number of cargas (of 300 lbs. each) of ore reduced in 1854 }	53·895	37·982	2·386
Ounces of quicksilver lost for each \$8·00 of silver produced }	4·97	12·74	...

Salt, it will be observed, is a large source of expense, since it has to sustain a land carriage of 300 miles; so that its cost at the mine is 16*l.* 10*s.* 8*d.* per ton. During the five years ending December 31st, 1857, the mines of this company produced silver to the value of 2,364,760*l.*

III.—AMALGAMATION IN COPPER KETTLES.

This system of amalgamation is principally employed in South America, and is only in use for the treatment of ores containing silver in a native state, or as bromide, chloride, or iodide, and in cases where these ores are comparatively rich. The consumption of some fuel is necessary, and hence in some localities the system cannot be employed.

The ores are first brought to the condition of a very fine powder, and in some cases concentrated by washing, and then thrown, with a considerable quantity of water, into kettles with copper bottoms, under which a fire is made, and the contents of the vessels brought to a boiling temperature.

From 10 to 15 per cent. of common salt is now added, and well mixed with a wooden stirrer. When salt is dissolved, an amount of mercury, somewhat inferior to the quantity of silver present, is placed in the kettle, and the stirring and heat continued.

From time to time the amalgam is examined, and its appearance indicates to the workman the necessity of adding more quicksilver, and the time to terminate the operation.

The results of the manipulations in the kettle are, an earthy residue, and the compound of quicksilver and mercury. The former often still holds enough silver to

be given over to the *amalgamation in heaps*, and the latter is distilled in an iron retort, in the manner described in the foregoing section, producing mercury that is given back to the process, and silver that is fused, refined, and moulded into ingots for sale.

The time required for this operation varies from five to six hours, and the loss of mercury is usually somewhat less than the amount of silver gained. In this respect therefore the system of amalgamation in kettles gives better results than the amalgamation in heaps.

CHAPTER XIV.

THE TREATMENT OF SILVER ORES AND ARGENTIFEROUS PRODUCTS BY THE
 "WET WAY"—ZIERVOGEL'S METHOD—AUGUSTIN'S METHOD—VON
 PATERA'S METHOD.

THE processes by which silver is obtained from argentiferous ores and products by the "wet way," or by "solution and precipitation," are all of quite modern origin. They belong to that last period in the history of metallurgy during which the science of chemistry has played such an important part.

The seed from which these processes sprang was planted, however, in the days of empiricism. Were my space less limited I might commence with the experiments made by Medina among the Cordilleras, in the middle of the 16th century, and trace in unbroken sequence the growth of process out of process, until I arrived at the systems introduced within the latter half of the present decennium, some of which have not yet been described upon the pages of a metallurgic treatise.

The methods in question have in most instances where now in use, supplanted the old plans of amalgamation and liquation (see page 204), and hence they show themselves generally adapted for such ores and products as may be treated by those methods. As a rule they are used for those containing little lead, and such as are largely cupreous.

With such ores, and under certain circumstances, the methods of extracting silver by the wet way are extremely advantageous. They exceed the plan of amalgamation in necessitating no loss of valuable mercury, and in the quickness and completeness with which the metal may be obtained from the mineral treated, and also in their being healthier for the labourers engaged upon them. They are far more economical than the plan of fusion with lead, in the item of fuel, in the time required, and in the amount of the various metals lost, while they are superior to the process of liquation in requiring less time and fuel, in accomplishing a more complete separation of the copper and silver, and in allowing the production of a copper of an excellent quality.

AUGUSTIN'S METHOD OF EXTRACTING SILVER WITH SALT WATER.

This plan of treating argentiferous ores and products was introduced by one of the officers of the Mansfeld Mining Company, at the Gottesbelohnung furnace, near Eisleben in Prussia, in 1849. It was retained but a short time, although exceeding in simplicity and cheapness the system of liquation and amalgamation, both of which it succeeded.

In its place the remarkably simple plan of Ziervogel,

which will claim our attention in the next section, was introduced. It is, however, at present in use at Freiberg in Saxony (where I was afforded every opportunity of studying it), and in Hungary, and its simplicity and certainty would recommend it for introduction in many localities where other processes are now employed.

The method of Augustin rests upon three circumstances, all of which have already been noticed. 1st. By subjecting an ore of silver to the proper roasting in connection with common salt (chloride of sodium) the precious metal may be converted into the chloride of silver. 2nd. A concentrated and hot solution of common salt will dissolve the chloride of silver in quantities depending upon its temperature and its concentration (see page 33). 3rd. Copper placed in an argentiferous solution of the chloride of sodium will precipitate the silver in a metallic form.

At Freiberg in Saxony, the system is employed for extracting the silver from a rich copper matt or regulus formed in the course of smelting the cupreous ores. This regulus is concentrated by repeated roastings and fusions until it contains an average of 69 to 70 per cent. of copper, and $\frac{4.2}{100}$ per cent. of silver. It holds further, a small amount of iron, antimony, arsenic, and other impurities.

In order that it may be properly roasted, it is first necessary to bring it to a very fine powder, which is done by breaking the cakes of regulus with hammers, and then crushing the pieces beneath iron stamps, and grinding in the usual manner. In this way a powder is obtained, which is carefully passed through a fine brass sieve.

Roasting.

The sulphide is now in a condition to carry to the roasting furnace. This is of the reverberatory class; the fuel is stone coal, and one attendant is sufficient to carry on the work. Four hundred weight are placed on the hearth at a time, and the fire, commenced at a moderate strength, is increased gradually while the powder is stirred frequently that every portion may be exposed to an intense heat. At the end of eight hours the proofs of complete roasting begin to appear; the powder becomes brown and earthy; the heat does not produce that interior glow which is an evidence of the presence of sulphur, and no fumes of sulphurous acid are to be perceived. The contents of the furnace are now drawn out and allowed to cool, and carried to a mill resembling that generally adopted for grinding corn, and after being brought to an extremely fine powder, are passed through a bolt and brought to the furnace to be subjected to the *chlorising roasting*. The copper and iron exist at this period chiefly in the form of sulphates, while the silver has been changed into a sulphate or into a metallic condition.

The powder is placed in the same furnace in which it was previously treated in charges of 3 cwt. and roasted for a short time. It is then mixed with 5 per cent. of common salt and roasted and stirred for about three hours. During this period the chloride of sodium is decomposed by the sulphuric acid of the sulphates, and chlorine set free, which combines with the silver, and nearly if not quite all of the precious metal takes on the form of a chloride. The powder is now removed from the furnace and conveyed to the department of lixiviation.

Lixiviation and Precipitation.

An elevated apartment is devoted to the lixiviation of the powder in which the silver has been brought to the condition of a chloride by the process above described. The vessels employed for the purpose are arranged in the manner shown in Fig. 75. Along the side of the

Tub used for lixiviation in Augustin's method.

second story are arranged a number of vessels *a, a, a, a*, &c., that are employed for lixiviation; they receive the powder, and in them the process of dissolving the chloride of silver takes place. The construction of each of these tubs may be understood by a reference to Fig. 74, in which the vessel is represented with the quarter nearest the spectator cut away. Upon the bottom, *a*, is laid a wooden cross, *b*, upon which comes a perforated disc of board, *c*. Upon the top of this is placed an even layer of twigs, *d*, and lastly, above this is brought a linen cloth bottom, which is made tight against the walls of the vat by being stretched upon a hoop. The

space *A*, above the filter, is filled with the substance to be treated, and the filtered liquor falling upon the bottom flows out through the cock, *h*. Each of the vessels is 3' 9" high, 2' 8" in diameter above, and 2' 4" below.

The eight tubs, *a*, *a*, *a*, *a*, &c., Fig. 75, are filled with powder, 8 cwt. being placed in each. Hot brine is now

Arrangement of tubs in Augustin's process of extracting silver.

allowed to flow from the basin, *s*, through the trough, *w w*, and conducted upon the powder in the tubs through the little tubes, *t*, *t*, *t*, &c. The fluid coming in contact with the finely-divided chloride of silver, dissolves it, and carrying it through the filter, flows off by a proper series of tubes to a reservoir placed above the tub, *b*. Here the particles of powder that may remain in mechanical suspension are allowed to settle, and the fluid passes into a series of vessels represented by *p*. These (as well as *c* and *d*) are furnished with double bottoms and filters. In *p* is placed a layer of *cement copper* 6 or 7 inches deep. The silver of the liquor is here precipitated in a reguline form, and the

copper takes its place. The fluid, falling from *p* into the vessel *c* is brought into contact with a second bed of copper as a means of securing a precipitation of all the silver. The cupreous fluid now falling into *d*, meets with metallic iron, which in its turn goes into solution and precipitates metallic copper. The brine, thus freed of its silver and copper is pumped into the reservoir, *s*, to be re-heated and used again. The cement copper from *d* is given back to *b* and *c*, and is thus made to serve several times. Hot brine is passed through the tubs, *a*, *a*, *a*, &c., in the manner just described, until a bright copper plate is not coated with silver when held in the stream flowing from them. The mineral remainder, which consists chiefly of the oxide of copper, is removed from the tubs to give place for a new charge, and assayed for its silver. When found to contain more than $\frac{1}{33}$ per cent., it is sent again to the reverberatory furnace, re-roasted, and again lixiviated. If it contains less than $\frac{1}{33}$ per cent. it is fused at once for copper.

The *cement silver* in the form of a fine crystalline powder that collects in the tubs *p* and *a* is taken out every eight or ten days, cleared of its particles of copper by treating it with hydrochloric acid, and placed in a vat, where it is washed by allowing water occasionally to flow over it. It is then removed from the vat, pressed into small balls, dried thoroughly, and taken to the refining department, where it is fused and purified for the Saxon mint.

The use of the method of Augustin is at present on the Continent confined to the treatment of concentrated cupreous furnace products ; but it is nevertheless applicable to the extraction of silver from its ores. It

may be employed where the metal is combined with sulphur, antimony, or arsenic, and where peculiar local circumstances exist, such as a scarcity of motive power, and an abundance of salt.

ZIERVOGEL'S METHOD OF EXTRACTING SILVER WITH WARM WATER.

As the process of Augustin may be looked upon as a modification of the European plan of amalgamation, in which the chlorising roasting is retained, and a new plan of solution and isolating the precious metal is introduced, so the process of Ziervogel may be considered a modification of the method of Augustin, in which a different kind of roasting and a new solvent is adopted. But notwithstanding this general connection of the methods of Ziervogel and Augustin, the various processes proper to each are so near and so ingeniously joined to one another, that we cannot withhold an expression of admiration for the skill of both inventors.

Augustin had hardly succeeded in displacing the time-honoured plan of amalgamation at the works of the Mansfeld Company, when a fellow officer, Hüttenmeister Ziervogel, advanced the simpler and cheaper method known by his name; and since 1857 this plan has been exclusively employed. At the time of my visit to the works, in the early part of the past year, all the silver produced by the company, amounting to 13,385 pounds annually, was extracted by this plan. A description of its various features will be found in the "Metallurgy of Copper," and hence it is not necessary to enter upon details here.

Its value, when compared with other systems of extracting silver from copper, as they have been succes-

sively employed at Mansfeld, will be perceived by inspecting the following table. The silver exists with the copper in the proportion of 1 part in 200.

	Cost.	Amount of silver left in copper.
	Thalers.	per ct.
Extracting the silver by liquation, from 1 cwt. of copper	10	$\frac{1}{10}$
„ „ amalgamation „ „	$5\frac{1}{2}$	$\frac{1}{17}$
„ „ Augustin's method „ „	$4\frac{1}{2}$	$\frac{1}{17}$
„ „ Ziervogel's method „ „	$2\frac{1}{2}$	$\frac{1}{34}$

The method of Ziervogel is founded upon the circumstance that when a powdered sulphide of copper and iron, containing silver, is roasted with proper precautions in a reverberatory furnace, the iron and copper pass first into the condition of sulphates, and then into oxides, and subsequently the silver undergoes the same changes, and if the heat be continued, will be transformed into a metallic condition. If the attendant arrest the process just at the moment after the copper and iron have reached the condition of oxides, and the silver has just become a sulphate, but has not yet begun to lose its sulphuric acid, he will obtain a mass in which the silver is in a form soluble in water, while nearly all the remainder is insoluble in that fluid.

If now, the process of lixiviation and precipitation be accomplished in a manner similar to that detailed in the last section as in use for the method of Augustin, but with hot water instead of hot brine as a solvent, the silver may be extracted almost entirely from the roasted powder and collected as cement silver.

The process of Ziervogel is adapted to the require-

ments of but few localities. It can only be carried out with success where the ores are of a pure and unvarying character, as is the case with those extracted from the beds of the Kupferschiefer, at Mansfeld. Very skilful and intelligent workmen are required, since the preliminary roasting is one of the most delicate operations in the metallurgy of silver.

VON PATERA'S METHOD OF EXTRACTING SILVER WITH THE HYPOCHLORITE OF SODA.

The history of the process of Von Patera is not less interesting than that of the plans of Augustin and Ziervogel. Invented and introduced a number of years after the more recent of these methods, it yields to the tendency of modern experiment, and departs still wider than either from the ancient metallurgic routine. Like the two methods above named, it consists in, 1st, roasting; 2nd, dissolving the silver; 3rd, precipitation; 4th, refining the argentiferous mass and preparation for the mint.

The *roasting* has the same object as that accomplished in the European amalgamation, and in the process of Augustin, viz., the conversion of all the silver into a chloride, but the apparatus employed is novel, and especially adapted for the treatment of very rich ores.

The *dissolving* is accomplished by a solution of the hyposulphite of soda ($\text{NaO}, \text{S}_2\text{O}_2$), a rare salt, possessing a remarkable power of forming a soluble compound with the chloride of silver. Its employment in the extraction of the precious metal from its ores or other compounds was first suggested by the distin-

guished English metallurgist Dr. Percy, in a paper published in 1848, a translation of which reached the Austrian chemist.

The *precipitation* is peculiar to this metallurgic process. The silver is thrown down as a sulphide by the polysulphide of sodium, which is added with great care, so that precisely enough may be added to throw down all the silver.

The *reduction* of the sulphide of silver thus obtained is readily performed in a retort, and the product refined for coining.

During a recent visit to the mines and furnaces of Joachimsthal, I was given every facility for studying this system, which was put in operation in 1858, and up to this date has produced about 4000 lbs. of silver.

The ores of Joachimsthal are remarkable for the numerous mineral species composing them. More than 100 varieties have been described as occurring in the veins from which the precious metal is procured. Among these may be mentioned the various compounds of copper, lead, bismuth, iron, nickel, and cobalt, with sulphur, oxygen, arsenic, and antimony. The remarkable richness of these ores has heretofore been adverted to. When the entire quantity delivered at the furnace is reckoned, the silver is found to compose 2 to 3 per cent., and many hundred weight are worked from which 5 to 8, and even as much as 14 per cent. are extracted. The fuel used at the furnace is brown and stone coal, wood, and charcoal. The first is moderately cheap, the second dear, and the third and fourth are becoming less abundant each year. Labour, on the other hand, is abundant, good workmen receiving only 1s. to 1s. 4d. per day.

The ore is in part prepared by hand sorting, and part by concentration upon the *percussion table*. It is delivered to the furnace in a powdered condition, and stored in appropriate magazines until required.

The first operation to which it is subjected, is

Roasting.

This process is performed in a reverberatory furnace, which presents several peculiarities that recommend it to the attention of the metallurgist. The usual long narrow hearth and fire-bridge, and short fireplace is here replaced by a hearth 9 ft. 9 in. across, and 6 ft. in the direction taken by the flames on their way from the fuel to the chimney. The fireplace, instead of being 2 ft. across, as is the case with many English furnaces, is here but 6 inches, and the grate upon which the fuel is consumed, instead of passing along about $\frac{1}{3}$ of the side of the furnace, as is often the case, is here $\frac{4}{5}$ as long as the hearth. The advantages secured by this arrangement are obvious to one observing the action of the furnace. The broad and short hearth makes possible an equal and high heat throughout the whole furnace, and the long fireplace allows no portion of the charge to remain in remote corners, beyond the reach of the intense fire, while the narrow fire-bridge absorbs less heat, and allows the flames to have a more direct action upon the contents of the hearth, than where a broad mass of bricks intervenes between the consuming fuel and the mineral that is being treated.

A further important innovation distinguishes this furnace from others of the same class. The fire-bridge is a tube of iron covered with clay, and having eight to

ten small openings in the side toward the hearth. A boiler attached to the furnace, but heated by a separate fire, produces steam of the pressure of about 4 lbs. to the square inch, which can, at the will of the operator, be conducted into this tubular fire-bridge, and allowed to stream out from the openings upon the roasting charge.

The powdered ore as it comes from the mine, is placed in the furnace in charges of 4 cwt. It is subjected to a slight fire at first, which is gradually increased, but not to a point high enough to induce clotting. Vapour is not admitted at first, but when the charge has arrived at a red heat, the pipe connecting with the boiler is opened, and as much vapour allowed to pass over the heated ore as is possible without decreasing the temperature below the point necessary for the proper chemical changes to go forward. In four hours the process is complete, and the ore is drawn, permitted to cool, and carried to a mill, where it is ground to fine powder, being at the same time mixed with some salt. It is then brought to the roasting furnace to undergo what is known as the *good roasting*. Three hundred weight of ore are here treated at once, being first intimately mixed with 6 to 12 per cent. of common salt, and, at the same time, with 2 to 3 per cent. of iron vitriol. This mixture is spread upon the hearth; in about an hour after being brought under the influence of the fire a red heat is reached; the vapour is then let on as before, and stirring commences. The fire is gradually made stronger, and in from six to sixteen hours—depending upon the value of the ore—the process is concluded.

The object of adding salt is to form with the silver a

chloride. The vitriol furnishes a means of decomposing the salt when not enough sulphides are otherwise present, and steam makes the combination of the chlorine and silver more certain, and by condensing the vapours that pass into the chimney and condensing chambers before they can reach the open air, enables the catching of nearly all the silver. Were it not for this contrivance, 10 per cent. of the silver would be lost, which would evidently make the treatment of rich ores by this means impracticable.

The roasted ore, still in a finely powdered condition, is transported to the apartment devoted to lixiviation, where the various apparatuses for solution and precipitation are arranged, as is shown in the accompanying cut, which gives a vertical section from one end of the building to the other, and which will be understood by reference to the following description.

First Lixiviation.

The powdered ore now contains the silver, as a chloride, and hence insoluble in water, while some of the nickel, cobalt, zinc, iron, copper, &c., are present, as sulphates and chlorides, and soluble in that fluid. Charges of 4 cwt. are thrown into the row of tubs represented by A, which are made of pine wood, well hooped with iron, and furnished with a filter, *a*, at the bottom. Water at as high a heat as possible is thrown upon this ore for about six hours, and thus all the soluble salts are taken into solution, and carried through the filter, *a*, into the trough, *b*, to appropriate vessels, where they are precipitated with lime-water, and if rich enough in silver, are collected and sent to be fused in a cupola furnace.

The fluid falling into *b*, is occasionally tested with the sulphide of sodium, and when no precipitate appears, the first lixiviation is deemed ended, and cold

Fig. 76.

Arrangement of apparatus employed in Von Patera's process of extracting silver.

water is thrown in to diminish the temperature of the ore, which must not be submitted to the next treatment until quite cold.

Second Lixiviation.

The powdered ore thus disencumbered of the several salts, soluble in pure water, is now thrown into the tubs, represented by B, which are also constructed of pine, and resemble in their interior arrangement the vessel used in Augustin's process, as figured at page 187. Of these vessels, seven are employed in the establishment at Joachimsthal. They are placed on a level with the vessels, A, and between the two rows passes a small railway, upon which runs the car, c. The vessels, B, are placed upon a small wagon, *w*, that can be run from the position shown in the cut to the car, c, and then carried backward and forward, and brought into close proximity with any of the tubs in the row, A. The vessel, B, having received 2 cwt. of ore from one of the larger tubs, is set in its place and treated with the liquor intended to dissolve out the silver. This consists of a cold solution in water of the hyposulphite of soda ($\text{NaO}, \text{S}_2\text{O}_2$). This fluid is brought from an appropriate reservoir by the trough, *h*, and allowed to filter slowly through the mass. It takes up the chloride of silver in the form of a double salt, and conveys it in solution through the filter, *l*, and thence into the trough, *s*, whence it flows into the precipitating tubs, c and d. The rapidity with which the fluid will flow through the powdered ore depends upon its fineness, and the length of time required for extracting all the soluble silver in the tubs depends upon this mechanical circumstance, and upon the quantity of silver in the ore. The richest mineral brought to the extraction, which contains about 14 per cent., requires forty-eight hours, that

containing 1 per cent. requires twelve hours. The ores containing but 6 or 7 per cent. require but one lixiviation, which brings the remainder down to about $\frac{1}{6}$ of a per cent.; but the ores of higher value must be submitted to two lixiviations, with an intermediary roasting with vitriol and salt, before they can be reduced so far. The remainders are dried and given over to fusion in a cupola furnace. The charge in each tub, B, is known to be ready for removal when the liquor falling from it no longer contains silver, which fact is known by a trial with a solution of sulphide of sodium, a re-agent that will produce a dark colour when only a trace of silver is present.

Precipitation of the Silver.

The argentiferous liquor falling from the vessels, B, is conducted into the tubs represented by E, of which there are six, each holding about 40 gallons, and into those represented by D, of which there are four, each holding about 80 gallons. When one tub is nearly full, the trough carrying the liquor is changed to another, and the precipitation of the silver may commence.

The plan here adopted is an exact imitation of a delicate laboratory process, and it is worthy of remark, that the common workmen have attained such a facility in performing it, that they never fail in producing the desired result. The precipitant is the *polysulphide of sodium*, formed by calcining soda with sulphur, and afterwards boiling the product, when dissolved in water, with sulphur in a state of fine division. It is conveyed to the tubs in large stone jars, and poured into the argentiferous liquor, until all the silver is supposed to

be thrown down, stirring being vigorously carried on at the same time. The workman now dips a little of the clear liquor out in a glass tube, and adds polysulphide of sodium. If a dark colour is produced, it is a proof that silver is still in solution, and more precipitant is added from the stone jugs; if, on the contrary, no sulphide falls in the test-tube, it is a question whether too much sulphide of sodium has not been added to the tub; and to prove this, some of the fresh silver-holding liquor is added to an assay taken from the tub under treatment. If in this case a precipitate is formed (of sulphide of silver), the same fresh argentiferous liquor is added carefully to the tub, until no reaction of sulphide of sodium is produced. When this point is reached, all doubt that the whole of the silver has been precipitated and that no excess of the precipitant remains, is removed by the application of still more delicate re-agents—acetate of lead, to detect the excess of sulphide, and the solution of some chloride, to prove the presence or absence of silver. This exact condition of neutrality is essential to the success of the process, since the fluid from which the silver is thrown down is again given to the lixiviation, and the presence of sulphide of sodium in the tubs used for solution (B) would lead to the formation of an insoluble sulphide of silver, and hence would prevent the method succeeding. The process of precipitation, complicated as it may seem, requires the labour of two workmen only fifteen minutes for each tub, even when the largest vessels are treated.

The flocky precipitate is now allowed six hours to settle to the bottom, when the liquor above is drawn off by means of a syphon, and the dark sulphide of

silver, which exists as a slime, is drawn off through the spiles, *t t*, which enter at the lower part of the tub.

The liquor from the syphons is carried to a reservoir beneath the floor of the apartment, and thence pumped up to the level of the trough, *h*, to be again used in the process of dissolving. It is a curious circumstance in the history of this method, that no hyposulphite of soda has been added since the commencement of the operation, when 14 lbs. were dissolved as a beginning. The sulphide of sodium, when exposed to the air, forms a small quantity of the hyposulphite of soda, so that this essential salt enters the circuit when the silver is precipitated, and thus the solvent, instead of becoming weaker, is continually concentrating, and must frequently be diluted by the addition of fresh water.

Treatment of the Sulphide of Silver.

The precipitated mass from the tubs, *D* and *E*, is deposited in three-cornered bags of hempen stuff, and hung in the wooden frame, *F*, to drain. In about half-an-hour the dark mass, which, beside sulphide of silver, consists chiefly of sulphate of soda, is placed while still in the bags beneath a screw press, and the fluid that remains in it is forced out as completely as possible. It is then dried in a warm room, placed again in the filtering bags, and warm water thrown over it, to wash out the sulphate of soda. The sulphide of silver, thus freed of its soluble salts, is now dried a second time, and heated in a muffle, to which air has access. The sulphur burns out with the characteristic blue flame, and in about three hours the entire mass is almost entirely reduced to the condition of metallic silver, which

in some instances assumes the thread or wire-like condition that is frequently seen in specimens of native silver.

The last process, which consists of a fusion, is now accomplished. The metal is placed in a graphite crucible, of Passau or English make, to the amount of 300 lbs., and fused. The sulphur that still remains is removed by placing metallic iron in the fused metal, and thus inducing the formation of a ferruginous regulus, which rises to the surface and is skimmed off. The surface of the metal is then cleared by adding a mixture of bone-ash and wood-ashes, and the silver dipped out and poured into moulds. The silver varies in purity between .980 and .985, and is at once sent to the Imperial mint at Vienna.

The workmen who have charge of this apparently complicated process were formerly engaged in the smelting department, and have no knowledge of theoretical chemistry, yet the whole affair is carried forward with the utmost regularity, and but occasional attention is required from the superior officers. The cost of extracting a pound of metal from the ore amounts to about 9s. 9d., which is about 6s. less than the cost of separating the same amount of metal by the old process of smelting.

CHAPTER XV.

THE TREATMENT OF ARGENTIFEROUS COPPER BY LIQUATION — REFINING SILVER UPON THE HEARTH AND BY FUSION IN CRUCIBLES.

THE ancient method of treating argentiferous copper for the silver it contains, by *Liquation*, remains still in use in a few localities. In Saxony it is supplanted by the modern and less expensive system of treatment by the wet way; but in the Upper Hartz it may be still seen in full operation, the plans of Zirvogel and Augustin, and the European system of amalgamation, not appearing suited for the plumbiferous copper of that region.

The system of liquation is based upon the fact, that when copper containing silver is alloyed with a certain amount of lead, and heated above the melting point of the latter metal but below that of copper, the lead will become fluid and drain or sweat out of the mass, carrying with it most of the silver, and leaving behind an impure copper. According to Karsten, who studied this process with care, the lead and copper in the alloy from which the argentiferous lead is extracted, should be in the proportion of 11 of the former to 3 of the latter; and further, for every part of silver present there should be about 480 parts of lead. These proportions are only approximate. In the Hartz, *black copper* with about one-sixth of a per cent. of silver is treated with profit, though were only one-eighth per cent. present it would not pay to extract it.

The process begins by fusing the argentiferous copper with the proper amount of lead. This is done in a cupola furnace about $5\frac{1}{2}$ feet high, which is well heated, charged with a small quantity of lead, and afterwards with copper, and then again with lead, and so on alternately, a double charge being always allowed to fuse together and flow out before a second double charge has time to fuse. The proportions of lead and copper being determined beforehand, the alloy that flows out of the furnace contains the proper amount of both metals. It falls into an iron mould prepared to give it the required form, which is that of a disk, 18 inches in diameter, and 3 to $3\frac{1}{2}$ inches thick. These are rapidly cooled by throwing water upon them, and then laid aside until a number are ready for further treatment.

LIQUATION.

The liquation hearths are composed of two walls, A and A, slightly leaning toward each other, and capped with two smooth iron plates, B B, which incline toward a middle line and approach within a few inches along one of their edges, at *e e*. This long aperture is above the canal, *i*, between the two walls, which canal, passing from one end of the apparatus to the other, ends in the basin, *c*.

When the operation is to commence, the argentiferous disks of copper are piled upon the iron plates in the position shown in the cut at *d d d*, &c., and the apertures around them and the space between, filled with charcoal. The side plates of iron, *p p p*, are then put up, and, by means of a log of kindling material thrown into the aperture, *o*, the fuel above is ignited.

In from half to three-quarters of an hour, the rich lead begins to trickle from the disks, and falling between the iron plates, runs out into the basin, *c*. At first, the heat is kept moderate, that too much copper may not go over into the lead, but, as the lead drains out, a higher heat is given, by opening the damper of the flue, *f*, and throwing more wood into the aperture *o*.

Liquation Hearth used in the Hartz.

When, at length, the lead ceases to flow, the operation is known to be complete, the fire is allowed to go out, and the porous mass of copper permitted to cool.

The principal products that result from this operation are two, viz. :—

Rich lead, which is usually given over to the process of cupelling (see p. 153), where the silver is secured in a metallic condition, and masses of *spongy copper* (*Kiehnstöcke*), consisting usually of copper with 10 to 25 per cent. of lead, and from $\frac{1}{30}$ to $\frac{1}{6}$ of a per cent. of silver. When very rich, this product is again fused with

lead and brought to the liquation hearth ; but when containing but a little silver it is subjected to an oxidising process which is known as *Darren* or *sweating*.

SWEATING THE SPONGY COPPER.

This process has for its object the removal of a still greater quantity of the argentiferous lead from the copper. The furnace is so arranged that the masses may be piled beneath an arch like that of a reverberatory furnace, and above several long apertures like *o* in Fig. 77. While so arranged they are given a strong heat, and at the same time a brisk current of air is passed over them. The lead coming to the surface is immediately oxidised, fuses and falls into the canals below, while the copper unfused remains in its place.

The oxidised product thus obtained is reduced in a cupola furnace and cupelled for the silver it contains, while the copper with still $\frac{1}{15}$ to $\frac{1}{30}$ per cent. of silver, and 8 to 15 per cent. of lead, is purified upon a German hearth (see Rudimentary Treatise on the Metallurgy of Copper, page 170), and thus brought to a marketable condition.

THE REFINING OF SILVER.

The more or less pure silver produced by the various methods heretofore described, whether by cupellation, amalgamation, or precipitation, is subjected to a final fusion previous to being sent to the mint, or sold to the dealers in precious metals. The impurities with which silver is mixed when brought to the process, depend

upon the nature of the ores employed, and upon the process by which they have been treated.

Silver from cupellation has usually more or less copper and lead, and sometimes antimony, arsenic, and nickel. The silver of amalgamation is generally mixed with copper, antimony, and zinc. The cement silver usually contains copper, and that produced by precipitation with sulphide of sodium retains a notable quantity of sulphur. These impurities, with the exception of copper, injure essentially the malleability and the tenacity of silver, and two methods are in use among furnace-men for obtaining a product possessing the properties demanded by the coiner and artisan.

I. Refining upon a porous hearth in imitation of the cupelling of rich lead, a plan often adopted where the silver is very impure. This plan, however, differs from the cupellation in the fact that litharge and other oxidized products are not taken from the surface of the fused metal, but are allowed to be absorbed by the porous mass upon which the fusion is accomplished.

II. Refining in crucibles. This method is advisable when the silver to be refined is but slightly adulterated, but when much impurity is present it entails too large a loss of silver. In those instances where the silver is impure, and not much lead is present, a small quantity of that metal is added during refining, that its fusible oxide may dissolve the more refractory substances, and thus enable their ready removal.

I.—REFINING SILVER UPON POROUS HEARTHS.

Silver may be refined in a moveable hearth, and in a furnace similar to that employed in the English cupel-

lation (p. 162), but smaller and containing no apparatus for throwing air upon the fused metal, or in a furnace with fixed hearth and moveable vault; or beneath a muffle. The first-named plan is in use in England and in various parts of the continent, the second is adopted in different parts of Germany, and the last named is especially employed for treating the silver produced in the Upper Hartz, where about 21,000 pounds are annually refined.

The silver from the various royal furnaces is collected at the old mint at Clausthal and there refined; six days in the month being set apart for that purpose.

The *tests*, or small hearths upon which the fusion is performed, are prepared by heaping leached wood-ashes into an iron form, then cutting a hollow in the mass about 1 foot in diameter, and 3 to 4 inches deep. These are properly dried, and when about to be used are set in a furnace consisting of a bench of mason-work, with side walls to retain the fuel that is piled upon it. A fireclay muffle is placed over this *test* or cupel, and so arranged that the attendant may have access to the interior, and a stream of air may pass over the surface of the test. A strong fire of charcoal is now made around the exterior surface of this muffle, and the whole apparatus soon brought to a high heat. The silver, as it comes from the furnaces, is broken into fragments, and placed in the crucible to the amount of 40 to 50 pounds, the door of the muffle closed, and the metal allowed to fuse, which requires two hours. The door is now opened and the metal stirred with an iron bar, and thus subjected in all its parts to the oxidising influence of the air. This stirring is repeated several times during a period of two hours,

at the end of which time the refining is usually concluded.

The surface of the metal is at first quite dull, from the oxides (chiefly that of lead) which swim upon it; but these are gradually cleared away and absorbed by the porous ash of the cupel, and at length the surface assumes a mirror-like brilliancy. The proper degree of fineness having been reached, the silver is allowed to cool gradually, and when almost hardened, the surface is kept open by stirring, that loss by the violent escape of gas may not take place (see p. 27). Water is now thrown upon it, and after becoming quite solid the mass is taken out of the muffle, hammered into a convenient shape upon an anvil, the particles of impurities adhering to it cleaned away, and it is then ready to be transported to the mint.

The silver thus obtained is nearly pure, being .9948 to .9965 fine. During the five years between 1854-5 and 1858-9, 94.408 pounds of fine silver were produced from 101.559 pounds of silver of cupellation, indicating a loss of 7.05 per cent. in the process of refining. The cost of accomplishing this operation is about $2\frac{1}{2}d.$ per pound.

At Freiberg in Saxony, where the yearly production of silver is about 62,000 pounds, the refining is performed in reverberatory furnaces.

The hearth is made of marl, and is large enough to hold 10 cwt. at a time. The vault above is made moveable, so that the workman may have every opportunity of making the hearth perfect.

The mass of the hearth being well dried, the above-mentioned amount of silver is charged, and a good coal fire kept up for two or three hours, at the end of which period the silver is found fused.

A current of air is now directed upon it which sets it in motion, and exposes all parts to an oxidising influence; the impurities, which consist chiefly of lead, are thus fused, and absorbed by the porous hearth. Assays are taken from time to time, and when the silver shows a silky lustre and fine texture, which usually occurs in one and a half to two hours, it is quickly taken out of the furnace by means of iron ladles, and poured into iron moulds. The ingots thus formed, which weigh about 18 pounds, are taken to the Saxon mint.

Refining Silver by Fusion in Crucibles.

This plan is often adopted by establishments where but a small amount of silver is to be treated and where the metal contains but little impurity; in larger works, however, it is occasionally in use. The crucibles constitute one of the most important sources of expense in this process. Those formed of graphite or plumbago, and known as English and American, are considered the best, and command the highest price in the market. Crucibles of fire-clay are also often employed; these, although they are originally much cheaper, last but a short time.

At Przibram, one of the most important mining and smelting localities in Austria, the following plan is employed. The silver, as it comes from the cupelling furnaces, and possessing a fineness of $\cdot 940$, is broken into pieces by the hammer and thrown into Ypser crucibles in charges of from 300 to 600 pounds. The fire being started, in five or six hours the mass is fused, when a handful of a mixture of two parts of lixiviated ashes, and one part of bone-ash, is thrown

upon the surface. This substance absorbs the fluid oxides (chiefly the oxide of lead), and enables them to be skimmed away.

This operation is repeated with fresh material some sixteen or eighteen times in the course of sixteen or eighteen hours, when the silver begins to boil, and shows a clear mirror-like surface. About 2 oz. of a mixture of borax and saltpetre is then placed in the pot, and for a quarter of an hour a very strong heat given. The metal bath is then skimmed, the surface covered with powdered coal, and after another heating the process is completed. The silver is dipped from crucibles into moulds of iron washed with clay and cast into ingots, which are found by analysis to be almost pure silver. This plan of refining requires scarcely more than one-half the fuel that is used during the usual methods of purifying upon the hearth.

CHAPTER XVI.

THE TREATMENT OF ARGENTIFEROUS GALENA FOR LEAD AND SILVER,
AS PRACTISED IN FLINTSHIRE.

IN the foregoing pages—where it has been the endeavour to give, as far as is consistent with the compass of this work, a general view of all the methods of any importance, for treating argentiferous and plumbiferous ores and products—the single operations having a close analogy have been classed together without regarding the locality of their application. This rational and comprehensive plan has necessarily prevented the minute description of single establishments. In the

following chapter, however, I desire to furnish the reader with an outline of the various processes adopted in an English furnace in the treatment of an ore of silver and lead, for the production of the two metals in a marketable condition.

Ores, fuels, fluxes, building materials, and wages.

The English ores brought to the Flintshire furnaces are usually mingled with a small quantity of carbonate of lime or sulphate of baryta, but yield to the assay 70 to 78 per cent. of lead, and 8 to 12 ozs. of silver to the ton. These ores are generally bought by the managers of the furnace at prices based on the current value of lead. The fuels are coke and coal, both of which are of good quality, and can be procured at a moderate price. Lime is the flux chiefly employed; it is abundant and cheap. The building material is principally brick, and both the common and refractory varieties are made in the neighbourhood. The price of wages, however, when compared with that of continental lead regions, is quite elevated, but at the same time the skill and vigour of the workmen are superior to those similarly engaged beyond the Channel.

Method of treatment.

The succession of processes here adopted will be readily understood by the student of the foregoing pages. It includes the following principal operations—

- I. *The treatment of the ores in the reverberatory furnace, and reduction of the slags in the cupola furnace.*

- II. *Concentration of the rich lead by Pattinson's process.*
- III. *Cupellation of the concentrated rich lead by the English system.*
- IV. *Reduction of the litharge.*

I.—TREATMENT OF THE ORES FOR RICH LEAD IN THE REVERBERATORY FURNACES; AND REDUCTION OF SLAGS IN THE CUPOLA FURNACE.

The general construction of the furnace employed will be understood by a reference to figures, pages 107, 108. The charge, either in the form of a powder or in small pieces, as the ore may come from the washing-houses, is allowed to fall, to the amount of one ton, upon the hearth, which is hot from a previous manipulation. A strong decrepitation takes place at first, which makes it necessary to lower the draught in order to prevent the small particles from being carried up the chimney. When the decrepitation ceases, the draught is opened, and the oxidation of the sulphur goes on rapidly. This oxidation is continued for two hours, during which time the workman stirs the ore five times, in order to expose fresh surfaces to the chemical action of the air, and equalise the heating of the ore.

The doors are now closed, and the fire strengthened for about a quarter of an hour, when the sulphates are made to react upon the oxide and sulphide of lead, by a vigorous stirring, and the metal produced flows into the interior basin, *p*, where it remains covered with scoriæ, which prevents its volatilisation. When the metal ceases to collect, the doors of the furnace are opened, and a second oxidising roasting is accom-

plished, which is followed as before with a strong fire and a vigorous stirring, by which means still more lead is made to flow from the ore. This series of operations is repeated several times; the furnace becomes gradually hotter and hotter, until about five hours after charging nearly all the charge is in a fluid condition; the lead occupying the lowermost part of the interior basin, covered by a layer of fused sulphides and sulphates, mixed with the earthy impurities of the ore.

The doors are now opened, and powdered lime thrown in. This forms a solid compound with the material on the surface of the lead, and in this state is lifted off, and thrown higher up on the hearth. This operation is repeated until only lead remains in the basin.

The compound of lime is now roasted and treated for the lead it contains. In about an hour this process is completed, when the slag is taken from the furnace, and the lead remaining in the hearth drawn off into the exterior basin, *l*.

If the interior of the furnace requires repairs, they are now performed, and another charge thrown in. The lead in the exterior basin is freed of the regulus or sulphide that collects upon its surface, and purified by plunging sticks of green wood into it. The boiling produced by the escape of steam and decomposition of the organic material brings the impurities to the surface, where they are oxidised and readily removed by skimming.

It is possible to treat in this way about four charges in twenty-four hours, which requires the consumption of two tons of coal, and 320 to 340 lbs. of lime. Two workmen are continually in attendance at each furnace, and the shifts last twelve hours.

The chief products of the treatment are two, 1st, *Rich lead*, which is obtained to the amount of about 63 per cent. (when the ore has assayed 78 per cent.), and which contains silver to the amount of 10 ozs. to the ton; 2nd, *Slags*, weighing about $\frac{1}{4}$ as much as the charge treated, and containing by assay 40 per cent. of lead. The loss by volatilisation is found to be from 8 to 9 per cent. of lead.

The lead is moulded into pigs, and sent to be treated by Pattinson's process; the slags are sent to a cupola furnace to be reduced by the method next to be described.

The cost of treating a ton of ore by this process is about eight shillings, nearly one half of which is paid for labour.

Treatment of slags in the cupola furnace.

The slags resulting from the operations in the reverberatory furnace, we have seen, amount to 25 per cent. of the ore charged. They are in an agglomerated condition, but at the same time quite porous, being composed of lime, oxides of lead and iron, the sulphates of lead and lime, and some sulphides.

The ease with which lead volatilises makes it advisable to expose the plombiferous materials to the heat as short a time as possible, to fuse with great rapidity, and to provide extensive apparatus for condensing the fumes.

The cupola furnace employed is represented in the accompanying elevation and section (Fig. 78 and Fig. 79). The construction of this apparatus is somewhat peculiar; the breast wall, *a*, the hearth, *s*, and a portion of the back wall, *b*, are composed of cast-iron,

and the other portions, less exposed to the flames, are built of refractory brick. The charge is thrown in at *c*, and the chimney, *i*, leads to the apparatus for condensation. The cast-iron hearth, *s*, has an inclination of about 15 degrees toward the front, and when the furnace is in use, is covered with a layer about four inches thick of fine coke, through which the lead, reduced above, filters, and thence flows into the ex-

terior basin, *e*. The section of the furnace is a rectangle about 22 by 26 inches, and its height to the top of the breast-wall is about 4 feet. The air is furnished through the tuyère at *t*, by a nozzle $1\frac{1}{2}$ inches in diameter, and at a pressure of about $1\frac{4}{10}$ inches of quicksilver, so that about 15 lbs. of air are given per minute.

The charge is usually composed as follows—

Slag from the reverberatory furnace	. 1000 parts.
Ashes and hearth ends	 332 „
Rich slags	 50 „

About 4 tons of this mixture are given to the furnace in twenty-four hours, and at the same time 1000 lbs. of coke, the former being always thrown upon the back side of the furnace, the latter upon the front.

The two products of this fusion flow continually, the slags falling into the reservoir, *r*, and the lead collecting in the basin, *l*. The length of time a furnace is kept in action varies from two to three weeks. A furnace in good order will produce in twenty-four hours from 2000 to 2200 lbs. of lead, generally poor in silver, which is dipped from the basin and moulded into pigs, and slags with 5 to 6 per cent. of lead, that are sorted in order to secure the portion containing granules, and the poor portions thrown away. About one-fifth as much lead as is obtained in the form of ingots is volatilised, and carried by the draught through the chimney; a portion of this is caught by the condenser.

The apparatus for condensation is in some cases extremely extensive and complicated. The fumes rising from all the furnaces are conducted by a subterranean canal into a large chamber furnished with various dividing walls, that cause the gases to take a serpentine course. While passing through this chamber, a rain of cold water is continually thrown upon them, and the particles of the compounds of lead in suspension are caught by the water, and carried off. The gases are drawn through this winding passage by means of a large steam-engine, that puts in motion several immense wooden suction-pumps, and they are thrown in their cooled condition into a chimney, through which they pass to the open air. The water containing the condensed matter is passed into large basins, where the valuable portion is deposited in the form of a fine mud or slime. The water being run off, this material takes a certain consistency, and is then moulded into bricks, dried, and fused in a cupola furnace.

These condensed fumes consist chiefly of the car-

bonate and sulphate of lead, mixed with a little lime. About 50 per cent. of their weight is obtained in lead, which is almost free from silver. This lead is not treated for its silver, but is sold at once. The cost of treating a ton of slag is about 18s., and the lead gained by the process of condensation costs about 5l. per ton, showing that a considerable profit is secured by maintaining the apparatus of condensation, notwithstanding the large expense incurred by it.

THE TREATMENT OF THE RICH LEAD BY PATTINSON'S PROCESS.

The theory of this process, and the manner in which it is performed, has already been spoken of at some length in Chapter XII.

The products of the operation were shown to be a *very rich lead*, holding from 300 to 600 oz. to the ton, which is sent to the cupelling furnace at once—a *very poor or soft lead*, containing 1 oz. or less of silver to the ton, which is usually considered poor enough to be sent to market—and thirdly, the product obtained by skimming the fused metal, and the sweepings of the establishment, which, being quite impure, are treated separately in a reverberatory furnace, producing a rich lead that may be sent back to the concentrating kettles.

Rich lead, holding about 10 oz. to the ton, produces by concentration, for each 10,000 lbs. :—

284 lbs. of very rich lead, with about 320 oz. to the ton.

9570 lbs. of soft lead, for market.

Thus the loss of lead will be seen to be about $1\frac{1}{2}$ per cent., the loss of silver is 2 per cent., and the cost of

concentrating a ton of rich lead is, under some circumstances, 2s. 4d.

CUPELLATION OF THE RICH LEAD.

The rich lead produced by the concentration is now ready for the cupellation, which has for its object the separation of the silver from the lead. The method of accomplishing this separation will be found sufficiently described at page 161.

The products of the operation are *silver of cupellation* about .985 fine, which is subjected to an especial refining, and *litharge*, a portion of which contains 5 to 8 oz. of silver to the ton. The purest of this may be sold as litharge, or the whole reduced to lead, and sent to the concentrating kettles. The product of the last stage of cupellation is a litharge containing sometimes as much as 40 oz. of silver to the ton. This is invariably reduced to rich lead, and concentrated for the cupellation. A third product of this operation is the old cupels, which are impregnated with oxide of lead, and also contain some silver. This is treated in the cupola furnace for the metals it encloses.

The cost of smelting, labour, and superintendence, is about 2ls. per ton of rich lead cupelled.

REFINING THE SILVER.

This is done in a small furnace, similar in general construction to that figured at page 162, and used in the above-described operation of cupelling rich lead. About 480 lbs. are treated at once upon a bone-ash cupel, and each operation requires about six hours. The silver, with a fineness of .985 is brought to .998, and is now ready for the mint.

REDUCING THE LITHARGE.

The litharge produced by cupellation is usually reduced to rich lead, and brought again to the Pattinson process. Occasionally, as above remarked, a portion is sold in the condition of an oxide. The process of reduction, the general principles of which have been described in Chapter XII., is accomplished in a reverberatory furnace. The litharge, in a coarse powder, is mixed with 10 per cent. of stone coal in small pieces. The hearth of the furnace is elliptic, and is formed of a ferruginous sand, which, in order to prepare it for the charge, is agglomerated by a strong fire.

Three tons of litharge mixed with coal are introduced at once; and towards the end of the operation, which lasts about five hours, the workmen stir the charge thoroughly, that the litharge and coal may be brought into the most intimate contact. The lead produced is poured into moulds, and after cooling is carried to the kettles for concentration. The 3 tons of litharge produce about $2\frac{1}{2}$ tons of rich lead, and 12 tons can be treated in twenty-four hours. Besides the rich lead produced, about 3 per cent. of a sort of scoria is obtained, which is sent to the cupola furnace to be fused with the slags produced in the reduction of the ore.

The cost of reducing a ton of litharge is about 2*s.* 7*d.* of which nearly half is expended in labour.

In summing up the annual results of operating a furnace treating 21,000 tons of ore, containing an average of 78 per cent. of lead, and about 10 ounces of silver to the ton, Rivot (from whose excellent article on the treatment of argentiferous lead ores in Flint-

shire, most of the facts contained in this chapter were obtained) calculates the amount of lead lost to be 1·375 tons, and the amount of silver ore 2000 lbs; or, in other words, of the lead shown to be present by assay 8·39 per cent. is lost, and of the silver 24 per cent.

The cost of treating 2200 lbs. of ore is estimated to be as follows :—

	s.	d.
Labour and superintendence	8	3
Coal	3	0
Coke	0	9
Lime	0	4½
Bone ash and potash	0	0¾
Tools, repairs, miscellaneous costs	2	0
	<hr/>	
	14	5½

to which a considerable sum must be added for general expenses.

When the various expenditures of the furnace are considered, the following proportional figures are obtained, which will indicate at once how insignificant the cost of treatment is when compared with the amount paid for the ores.

Cost of ore	30 units.
Cost of smelting	1·5 „
Loss of lead	2·5 „
Loss of silver	1·0 „

CHAPTER XVII.

THE MANUFACTURE OF SHEET LEAD—LEAD PIPE—SHOT—WHITE LEAD
—RED LEAD—AND THE ALLOYS OF LEAD AND SILVER.

THE MANUFACTURE OF SHEET LEAD.

LEAD is obtained in sheets by casting the metal, in as pure a condition as possible, in plates 5 or 6 feet square and 4 to 6 inches in thickness, and then passing it many times between two large and nicely-turned rollers of cast iron. The distance between these two rollers is slightly decreased by means of screws, after each passage of the plate, so that the mass grows gradually thinner. In this way a sheet is at length obtained which may be 300 to 400 feet long, and 6 or 7 feet broad, and when intended for roofing, for which purpose it is frequently employed, it is cut by means of shears into lengths convenient for working, and thus sent to market.

Lead pipe was formerly made by a process having much resemblance to that of wire-drawing. A short and thick cylinder of soft lead was first cast, and this was drawn through a series of steel dies, each of which was smaller than the one immediately preceding, until the required diameter was reached. A mandril of steel was always retained in the interior of the tube, to keep the opening of the proper size. Good pipe was made in this way, but the operation was slow, and lengths of only 20 or 30 feet could be obtained.

The plan now employed for making lead pipe is much more expeditious. The apparatus consists of a very

strong iron cylinder, furnished with a massive piston at one end, and at the other with an aperture just the size of the exterior diameter of the required pipe, in the middle of which is secured a smooth steel mandril, whose diameter is exactly equal to that desired for the pipe. The cylinder is kept hot by a fire around its exterior surface. When this apparatus is to be used the cylinder is filled with lead, and by means of a strong hydraulic press the piston is forced into the cylinder, and the lead driven out at the opposite end in the form of a smooth tube. At the royal manufactory of Saxony, tubes from $\frac{1}{4}$ of an inch to 6 inches interior diameter are thus pressed, and are furnished in lengths varying from 50 to 100 feet. These tubes will bear a pressure of from 1 to 3 atmospheres with security.

THE MANUFACTURE OF SHOT.

The lead used for making shot, in order that the grains may have a perfectly spherical form, should always contain a certain quantity of arsenic. It is necessary to add from $\frac{3}{10}$ ths to $\frac{8}{10}$ ths per cent. of this substance to the leads of commerce. Much of the metal used in this manufacture is produced from impure ores, and is largely antimonial; in cases where much of this substance is present, a larger quantity of arsenic is required.

The lead is fused in an iron pot in quantities of 2 or 3 tons, and mixed at the same time with the proper proportion of arsenic. The fused metal is then poured into a sort of sieve, formed of thin plate pierced with numerous perfectly round holes. These sieves are placed at the tops of high towers, or above deep pits, so that the drops of lead falling from them may have an opportunity of cooling and becoming hard in the course

of their passage downwards through the air. At the bottom of the tower or pit is a large tub of water, into which the grains fall, and from which they are collected from time to time, and after being polished by placing them in a cask with a small quantity of graphite, and giving the cask a rotatory motion, they are ready to be sent to market.

METHOD OF MAKING WHITE LEAD.

White lead, the most important colouring matter used by the painter, is composed of 112 parts by weight of lead, and 22 of carbonic acid. It mixes readily with oil, and may either be used alone or mixed with substances that serve to give it any desired tint.

Holland was for a long time the only country in which this substance was largely produced, but within the last half-century large manufactories have been started in various other parts of Europe and in the United States.

Nearly all the white lead of commerce is made by what is known as the Dutch method. This consists in exposing thin plates of lead to the air, acetic acid, vapour of water, and carbonic acid, at a temperature of from 107° to 140° , and then collecting and preparing for market the compound resulting from the chemical action so brought about.

When exposed as above, the lead is first oxidised. It then becomes a tri-basic acetate; this is decomposed by the carbonic acid, which carries off a portion of the base, producing a neutral acetate, which in the presence of fresh oxide of lead again becomes a tri-basic salt, again to be decomposed by the carbonic acid. This process continuing, a large portion of the carbonate is at length obtained.

In practice, the lead is first fused and cast into plates several lines in thickness, and weighing about 2 lbs. Each of these plates is rolled into a scroll, and placed in an earthen pot, into which has been poured about a pint of vinegar. These pots are then set in layers, alternating with stable manure or spent tan, in a chamber of masonry prepared for the purpose, each layer being kept separate by pieces of scantling placed so that air may have access to the pots. The fermentation of the manure or tan produces the requisite heat, and the chemical action soon sets in, and in from thirty-five to forty-five days, the transformation of the lead into the carbonate has reached the desired point.

The scrolls of lead are then taken out of the pots, and the carbonate, which adheres in the condition of scales, is detached by bending the plate in various directions, and beating it with an instrument of wood. The carbonate is then mixed with water, ground very finely, and dried. It is usually subjected to a subsequent grinding with oil, and is then ready for sale.

THÉNARD'S PROCESS OF MAKING WHITE LEAD.

This method was at one time employed at Clichy, near Paris, but the paint produced was found to be of a quality so inferior to that produced by the plan above described, that it has been relinquished.

By this plan, litharge was dissolved in acetic acid, formed by the destructive distillation of wood. This solution was then run into larger basins of wood, lined with copper; and carbonate acid gas, produced by the combustion of charcoal or coke, was passed through, and thoroughly brought in contact with every part of the liquor. After the action of the carbonic acid had been

continued a sufficient time, the carbonate of lead which it formed, was allowed to settle to the bottom, and the liquid above was decanted. The precipitate of carbonate was then prepared by drying and mixing with oil for the market.

The carbonate of lead, usually found in commerce, is rarely pure. It often contains the sulphate of baryta, or heavy spar, the sulphate of lead, and occasionally chalk. The chalk may be detected by dissolving the paint in nitric or acetic acid, and precipitating the lead with sulphide of soda. If chalk is present, it will now give a white precipitate, if oxalic acid be added to the fluid. The sulphate of baryta and lead do not dissolve in acetic and nitric acids, and hence it is only necessary to observe whether there is a remainder when the commercial article is treated with those re-agents.

THE MANUFACTURE OF MINIUM OR RED LEAD.

The compound of the protoxide and the peroxide of lead ($2 \text{PbO} + \text{PbO}_2$) is a common substance known as red lead. It is made by oxidising the protoxide of lead, or litharge, by heating it in contact with air. The materials used for this purpose must be of the purest quality since but a small admixture of the oxide of copper spoils the product for many uses. The leads of England, Spain, and America are often pure enough to be employed at once in the fabrication of red lead, but many sorts require that a preliminary refining be accomplished. This is done by a process of calcination resembling that described at page 144, or by fusing a considerable quantity of metal in a pot, and after stirring it and allowing it to settle, pouring off the upper third of the mass, which will be found to carry with it most of the copper

and other deleterious impurities. This purified lead is now placed in a reverberatory furnace and oxidised, the product as in the case of cupellation, being the protoxide of lead, or litharge. This is then ground in a mill and carefully sifted, so that a fine powder is obtained, which is placed in an iron box and set beneath the arch, or spread directly upon the floor, of a reverberatory furnace, and oxidised by allowing air to pass over it while in a heated condition. It thus goes over into the minium, or red lead of commerce.

Mine Orange is only a pure variety of minium, obtained by the calcination of the carbonate of lead. Minium is frequently adulterated with the red-oxide of iron, and with brick dust. These are readily detected by heating the suspected sample strongly, where the minium becomes yellowish, while the brick and oxide of iron remain red.

THE ALLOYS OF LEAD.

Lead forms alloys with a large number of the metals, and several of the compounds thus formed are considerably employed in the arts.

The compound of *lead* and *tin* is harder and tougher than the latter metal, but less brilliant. The *solder* of the plumbers is formed by fusing together equal parts of these two metals: 8 parts of lead and 92 of tin form a compound suitable for making spigots and plates: 20 parts of lead and 80 of tin produce an alloy suitable for making spoons, candlesticks, and inkstands.

TYPE METAL is an alloy of lead and antimony, the proportions used being different for different sorts of type. Large and soft type are made of 7 of lead and 1 of antimony; 6 of lead and 1 of antimony are also

employed for making a large sized type; and 4 of lead and 1 of antimony is used for very small type. Stereotype metal is usually formed of from 4 to 8 parts of lead and 1 of antimony. To this are added a little bismuth, tin, and sometimes a little copper.

THE ALLOYS OF SILVER.

Silver enters into combination with more or less facility with a great number of metals, but its most important alloys are those formed with copper. With this metal it will unite in all proportions by fusion, forming a product less ductile but harder and more elastic than silver. This compound is hence better adapted for making money than pure silver, since more capable of resisting the continued friction to which a circulating medium is subjected. The standard English alloy of silver contains 222 parts of silver and 18 parts of copper; that of France consists of 900 parts of silver and 100 parts of copper. The process of making this alloy and coining it into pieces adapted for circulation is extremely interesting. The silver is bought from the bullion dealers in the form of ingots, weighing about 1000 oz. each; these are carefully assayed, and the amount of copper necessary to bring them to a proper standard is calculated. Cast or wrought iron pots, capable of holding about 420 pounds, are employed for melting. These are placed in a furnace and brought to a red heat, and the silver and required copper added, and at the same time sufficient powdered charcoal to cover the surface of the metal. The silver is soon fused, and when quite fluid, is thoroughly stirred with an iron stirrer, so that the whole mass may be brought to an uniform mixture. The pot is now removed by means of a crane, and carried

to a series of moulds, into which its contents are poured, thus producing ingots of the proper size and composition to be rolled for coining. These bars, after being carefully assayed, are given over to the rolling department, where they are passed repeatedly between two steel rollers, that are turned by machinery in opposite directions, and which are gradually brought closer to each other. The metal is rolled cold, but since after passing several times, and becoming much lengthened out, it is liable to crack on the edges, it is from time to time cut shorter and annealed, by heating in a reverberatory furnace and quenching with water. Having at length reached the thickness necessary for the coins, the ribands of metal are passed between two steel plates for the purpose of smoothing down all asperities.

The strips of metal are then given over to the cutting-out press, where by means of a steel punch, exactly the diameter of the piece required, worked by powerful machinery, disks are punched from the prepared ribands having as nearly as possible the weight of the coin it is desired to manufacture. The pieces have their edges raised or milled by a peculiar machine, and are subjected to another annealing, in order to soften them for stamping, before which last operation the oxide that may have collected on the surface is dissolved off by dilute sulphuric acid, and the pieces thus brought to a pure white colour.

Each piece is then subjected to a powerful compression between steel dies, upon which are engraved the devices which it is necessary for each coin to possess to make it legal, and with which every one is familiar.

The pieces of money thus formed are ready to enter into circulation as a medium of exchange.

CHAPTER XVIII.

STATISTICS OF LEAD AND SILVER.

It is impossible to make an exact estimate of the quantity of lead raised and smelted in the world, on account of the almost entire absence of reliable data from South America, Asia, and Africa. The production of these continents is, however, insignificant, when compared with that of Europe and North America. In 1854, Whitney estimated that 133,000 tons were raised, which were divided among the different countries according to the annexed table of actual and relative amounts :—

	Tons.	Relative amount.
Russia	800	·6
Sweden	200	·1
Great Britain	61,000	45·9
Belgium	1,000	·8
Prussia	8,000	6·0
Hartz	5,000	3·8
Saxony	2,000	1·5
Rest of Germany	1,000	·8
Austria	7,000	5·2
France	1,500	1·1
Spain	30,000	22·5
Italy	500	·4
United States	15,000	11·3
	133,000	100·0

The labours of Mr. Hunt, the indefatigable statician of the Royal School of Mines, at London, have enabled me to give with detail the yield of lead and silver in the various districts of the United Kingdom.

The following table will be found interesting, as showing *the quantity of lead ore raised, and lead made, with the quantity of ore required to make 100 tons of lead, and the quantity of lead contained in 100 tons of ore, in the United Kingdom, year by year, from 1848 to 1857 inclusive.*

	Lead Ore.		Lead.		Ore to make 100 Tons Lead.	Lead in 100 Tons Ore.
	Tons.	Cwt.	Tons.	Cwt.	Tons.	Tons.
1848 . . .	78,944	0	53,373	0	147·909	67·608
1849 . . .	86,823	0	58,715	9	147·871	67·626
1850 . . .	92,957	13	64,428	14	144·279	69·309
1851 . . .	92,312	4	65,289	6	141·389	70·726
1852 . . .	91,198	3	64,960	18	140·388	71·230
1853 . . .	85,042	18	60,968	12	139·485	71·691
1854 . . .	90,553	12	64,005	3	141·479	70·681
1855 . . .	92,250	16	65,691	5	140·430	71·209
1856 . . .	101,997	15	73,129	0	139·476	71·696
1857 . . .	94,479	18	67,441	15	140·090	71·382
Total . . .	906,559	19	638,003	2	142·093	70·376
Average . . .	90,656	0	63,800	6	142·093	70·376

STATISTICS OF LEAD.

The following Table, showing the quantity of lead ore raised, and of lead made, with the quantity of ore required to make 100 tons lead, and the quantity of lead contained in 100 tons ore, each year, from 1848 to 1857; also the total quantity and the average per year for those ten years, in England, Wales, Isle of Man, Scotland, and Ireland; will indicate at a glance the relative value of the several lead-producing districts of the United Kingdom:—

	TOTAL FOR TEN YEARS, 1848 TO 1857.				AVERAGE PER YEAR FOR THE TEN YEARS, 1848 TO 1857.			
	Lead ore raised.	Lead made.	Ore to make 100 tons lead.	Lead in 100 tons ore.	Lead ore raised.	Lead made.	Ore to make 100 tons lead.	Lead in 100 tons ore.
	Tons. Cwt.	Tons. Cwt.	Tons.	Tons.	Tons. Cwt.	Tons. Cwt.	Tons.	Tons.
ENGLAND:								
Cornwall . . .	92,356 7	61,310 16	150·635	66·385	9,235 13	6,131 1	150·635	66·385
Devonshire . . .	28,117 9	17,219 11	163·290	61·240	2,811 15	1,721 19	163·290	61·240
Cumberland . . .	87,497 4	61,167 18	143·043	69·908	8,749 14	6,116 16	143·043	69·908
Durham and Northumb- erland . . . }	210,943 17	156,469 19	134·814	74·176	21,094 8	15,647 0	134·814	74·176
Westmoreland . . .	9,812 6	7,326 19	133·915	76·673	981 5	732 14	133·915	76·673
Derbyshire . . .	78,735 13	51,075 18	154·154	64·869	7,873 11	5,107 12	154·154	64·869
Shropshire . . .	35,602 5	25,916 18	137·369	72·796	3,560 4	2,591 14	137·369	72·796
Somersetshire . . .	1,426 10	991 0	143·895	69·495	142 13	99 2	143·895	69·495
Yorkshire . . .	94,545 1	64,919 16	145·633	68·665	9,454 10	6,491 19	145·633	68·665
Total . . .	639,036 12	446,398 15	143·153	69·854	63,903 13	44,639 17	143·153	69·854

WALES:												
Glamorganshire . .	94	0	67	10	139·259	71·808	9	8	6	15	139·259	71·808
Caermarthenshire . .	10,217	4	7,391	15	138·217	72·350	1,021	14	739	4	138·217	72·350
Brecknockshire . .	24	0	20	0	120·000	83·333	2	8	2	0	120·000	83·333
Cardiganshire . .	68,885	6	49,532	11	139·071	71·905	6,888	10	4,953	5	139·071	71·905
Radnorshire . .	145	7	105	13	137·572	72·686	14	11	10	11	137·572	72·686
Montgomeryshire . .	15,166	8	10,630	7	142·671	70·091	1,516	13	1,063	1	142·671	70·091
Merionethshire . .	1,348	5	987	10	136·575	73·219	134	16	98	15	136·575	73·219
Denbighshire . .	12,129	15	9,374	0	129·400	77·279	1,213	0	937	8	129·400	77·279
Flintshire . .	78,442	5	58,199	4	134·782	74·193	7,844	5	5,819	18	134·782	74·193
Caernarvonshire . .	898	15	637	2	141·130	70·856	89	17	63	14	141·130	70·856
Total . .	187,351	5	136,945	12	136·807	73·095	18,735	2	13,694	11	136·807	73·095
ISLE OF MAN												
ISLE OF MAN . .	27,204	13	18,826	0	144·507	69·200	2,720	10	1,882	12	144·507	69·200
SCOTLAND . .	23,700	7	16,464	10	143·950	69·468	2,370	1	1,646	9	143·950	69·468
IRELAND . .	28,830	12	19,044	5	151·386	66·056	2,883	1	1,904	9	151·386	66·056
Sundries . .	436	10	324	0	134·722	74·226	43	13	32	8	134·722	74·226
Total . .	906,559	19	638,003	2	142·093	70·376	90,656	0	63,800	6	142·093	70·376

The entire produce of lead and silver in the United Kingdom in the year 1859 was as follows :—

	Lead Ore.		Lead.		Silver.
ENGLAND.	Tons.	Cwt.	Tons.	Cwt.	Ounces.
Cornwall . . .	7,842	15	4,985	12	215·964
Devonshire . . .	3,172	2	2,090	1	66·875
Somersetshire . . .	850	0	400	0	·950
Shropshire . . .	4,062	14	3,008	6	...
Derbyshire . . .	10,929	0	5,853	0	3·000
Yorkshire . . .	9,704	2	6,338	10	1·178
Staffordshire . . .	36	5	20	0	...
Westmoreland . . .	247	11	125	19	·431
Cumberland . . .	7,180	9	5,250	14	39·406
Cheshire . . .	160	2	69	17	·150
Durham and Nor- thumberland . . }	19,571	0	14,568	0	74·222
WALES.					
Caermarthenshire . .	913	0	637	10	1·700
Cardiganshire . . .	7,466	4	5,569	9	37·787
Radnorshire . . .	69	0	45	0	·125
Montgomeryshire . .	2,573	14	1,954	10	6·036
Merionethshire . . .	303	0	196	0	·962
Denbighshire . . .	5,076	0	3,981	10	14·318
Flintshire . . .	4,099	6	3,118	0	22·693
Caernarvonshire . . .	157	10	120	0	·480
ISLE OF MAN . . .	2,464	0	1,880	10	56·974
SCOTLAND . . .	1,942	9	1,347	9	4·022
IRELAND . . .	2,477	10	1,613	15	13·998
Sundries under 10 tons	83	5	60	0	·346
Silver from silver ore .	...		...		16·660
British mines . . .	...		...		...
Total from United Kingdom . . }	91,381	12	63,233	5	576·027

ESTIMATED VALUE OF LEAD AND SILVER CONSUMED IN GREAT BRITAIN IN THE
YEARS 1857, 1858, AND 1859.

	1857.	1858.	1859.
	£	£	£
Lead and silver produced in the United Kingdom .	1,656,668	1,645,574	1,564,332
Silver imported, 846,569 oz., 1857 * . . .	232,806		
” ” 750,000 oz., 1858 * . . .		206,250	
” ” 1,370,548 oz., 1859 * . . .			342,637
	1,889,474	1,851,824	1,906,269
	1857.	1858.	1859.
	Tons.	Tons.	Tons.
Lead exported . . .	22,088	19,555	20,491
Lead imported . . .	12,768	14,139	23,020
Balance of exports . . .	9,320	5,416	...
Balance of imports . . .	.	.	.
Value consumed . . .	.	.	.
	1,677,636	1,736,111	1,975,807

* Some part of this was obtained from argentiferous copper ores.

The exports of lead in the year 1859 were 20,491 tons, of which Russia, the United States, China, Australia, and Brazil, took the largest portion. This lead was chiefly in the form of pigs, sheets, and shot.

The imports during the same year amounted to about 24,000 tons, of which by far the largest portion, or 19,588 tons, came from Spain; Belgium furnishing the next greatest quantity, or only 1,301 tons.

The present silver produce of the world is probably

not far from 3,000,000 lbs. per annum. The following table gives the absolute and relative quantities furnished by the most important silver-producing countries on the globe, at three periods in the present century :—

	1800.		1845.		1850.	
	lbs.	Per cent.	lbs.	Per cent.	lbs.	Per cent.
Russian Empire	58,150	2·5	53,000	2·4	60,000	2·1
Scandinavia	...	...	20,000	1·0	20,400	·7
Great Britain	...	...	32,000	1·5	48,500	1·7
Hartz	...	...	32,000	1·5	31,500	1·1
Prussia	...	...	15,250	·7	21,200	·7
Saxony	141,000	6·	50,000	2·3	63,600	2·3
Other German States	...	...	2,000	·1	2,500	·1
Austria	...	...	81,500	3·7	87,000	3·1
Spain	...	...	108,200	4·9	125,000	4·4
France	...	...	7,500	·3	5,000	·2
Australia	...	...	...	...	10,000	·4
Chili	18,300	·8	90,000	4·1	238,500	8·3
Bolivia	271,300	11·6	139,400	6·4	130,000	4·6
Peru	401,850	17·2	303,150	13·9	303,150	10·7
New Granada	5,000	·2	13,100	·6	13,000	·5
Brazil	1,200	...	600	...	675	...
Mexico	1,440,500	67·1	1,235,000	56·6	1,650,000	58·4
California and United States	...	...	300	...	17,400	·7
	2,337,300		2,183,500		2,817,425	

A glance is sufficient to show the immense importance of Mexico as a silver-producing country, more than half the annual supply coming from that republic. Humboldt calculated that the silver brought to Europe from Mexico and South America between 1492 and the

breaking out of the Mexican Revolution in 1809, would form a solid ball $83\frac{7}{10}$ ths Paris feet in diameter.

The amount and value of silver produced from ores raised in Great Britain during the five years ending 1858, is shown in the accompanying table:—

	1854.	1855.	1856.	1857.	1858.
	OZS.	OZS.	OZS.	OZS.	OZS.
England . .	419,824	439,983	481,909	417,343	404,954
Wales . .	67,051	57,521	62,357	58,097	71,593
Ireland . .	18,096	7,252	3,700	3,071	14,361
Scotland . .	5,426	4,947	5,289	4,206	6,882
Isle of Man .	52,262	51,597	60,382	48,016	46,985
SILVER ORES .	...	...	...	...	4,250
	562,659	561,300	613,637	530,733	571,345
Value at 5s. 6d. } per oz. . }	£154,730	£154,357	£158,750	£146,501	£157,119

The tables below give a view of the silver and lead *ores imported* into the United Kingdom in 1859, with the ports at which they entered:—

	Tons.	cwt.	Value.
London	98	7	£ 5,240
Liverpool	1,666	14	102,998
Southampton	21	4	220
Swansea	4,664	18	234,179
	6,451	3	342,637

	LEAD ORE.	Cwt.
London		114
Liverpool		1,713
Berwick		107
Hartlepool		5
Newcastle		48
Hull		3
Swansea		109
		2,099

To this it is proper to add a table of the imports of silver ore into the United Kingdom for the four years previous to 1859, and a statement of countries from whence brought:—

	Quantity.	Declared Value.
	Tons.	£
1855.		
France	675	3,370
Brazil	135	13,575
Chili	7,546	541,888
Bolivia	80	4,660
Other parts	71	1,147
	8,507	564,640
1856.		
France	259	1,685
Cuba	125	9,960
Chili	5,997	340,432
Peru	135	1,991
Other parts	51	902
	6,567	354,970
1857.		
France	234	1,765
St. Thomas	14	1,450
New Granada	3	1,032
Chili	5,401	291,934
Peru	55	3,180
Other parts	4	150
	5,711	299,511
1858.		
New Granada	10	5,030
Chili	3,106	178,957
Peru	329	15,824
British Settlements in Australia	369	5,960
„ „ Honduras	60	2,310
Other parts	75	1,073
	3,949	209,154

The total amount of lead produced by the mines of Great Britain—

In 1858 was 68,303 tons, valued at £1,489,005 ;

In 1859 ,, 63,233 ,, ,, 1,410,095.

The total amount of silver produced by the mines of Great Britain—

In 1858 was 569,345 ozs., valued at £156,569 ;

In 1859 ,, 576,027 ,, ,, 158,407.

THE END.

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